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ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

BY

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PART I.

CHEMICAL PHYSICS.

SIXTH EDITION.

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TO THE SIXTH EDITION.

IN the present Edition, short notices of some of the most recent discoveries in those branches of Physics which are related to Chemistry have been incorporated in the work, and several new paragraphs have also been introduced, especially in the section on Polarization of Light, a subject which is becoming of great importance to the chemist in the study of many organic compounds.

An attempt has been made to bring the terminology into accord with the views of the present time, and in this the Editor has received much valuable assistance from his friend and former colleague, Mr. A. G. Greenhill, Professor of Applied Mathematics to the Advanced Class of the Royal Artillery Institution. Dr. Andrews has also very kindly revised and corrected that portion of the book which contains an account of his researches on the Heat of Combination and the Condensation of Gases.

Nearly all the references have been verified, and the year of publication introduced; it has also been found advisable to recalculate all numbers which were capable of such treatment, and thus many inaccuracies have been discovered and removed.

Cooper's Hill, August, 1877.

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TO THE FOURTH EDITION.

THE principal changes in this Edition consist in the adoption of the new system of Atomic Weights, with the method of notation dependent upon it; and the introduction of the Centigrade values for degrees of temperature, in addition to those on Fahrenheit's Scale, as well as of the Metrical Equivalents to the English weights and measures, employed in the description of processes and apparatus.

The use of barred letters to denote the symbols applied to the new atomic weights has been discontinued, as it is no longer necessary, inasmuch as the new values alone are employed in the present Edition.

There may be considerable difference of opinion as to the expediency of endeavouring to introduce the metrical system of weights and measures into the transactions of commerce, and the concerns of daily life. But there is a general and increasing desire amongst men of science to secure the adoption of some *uniform* system in the scientific writings of men of all countries. It would not be difficult to show that the metrical system has its defects. But it is founded upon principles that are simple, intelligible, and consecutive, and it is capable of convenient application. Moreover, and this is of special importance, it is widely adopted in various countries of Europe, as well as in North America, and the number of scientific men who employ it

is increasing yearly. There is, therefore, a probability that the metrical system will be generally used by men of science, and this can be said of no other system of weights and measures. I have, therefore, thought it right to introduce it side by side with our own, in order to familiarize the student with its units.

The volume has also received various additions of greater or less importance, such as the progress of science demanded. A considerable portion of the introductory chapter has been re-written. Among the larger additions may be mentioned an account of the researches of Deville and of Graham upon the permeation of metallic septa by gases, at elevated temperatures; and the results obtained by Gladstone and Dale, and by Landolt upon the connexion of the optical properties of bodies with their chemical composition. Considerable additions have been made to the Section on Spectrum Analysis; and the Chapter on the Photographic Actions of Light has been transferred from the second volume, in order that it may be considered along with the other phenomena of light described in the present part. Some account of the British Association standard of electrical resistance, as well as of the machines of Holmes and of Wilde for producing light by magneto-electric currents, will also be found in their appropriate places.

King's College, London, June 5th, 1867.

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TO THE FIRST EDITION.

THE work, of which the first part is now presented to the Reader, was originally designed to supply the Students who were attending the Course of Lectures on Chemistry at King's College with a text-book to guide them in their studies.

The present Part, on *Chemical Physics*, is devoted to a subject upon which no elementary work has appeared in this country since the publication of the excellent Treatise of the late Professor Daniell, and in attempting to supply what the Author, in his own experience, has felt to be a want, he ventures to hope that the result of his labours may be found useful to persons beyond the circle of his own immediate Class. Much new matter, which has never yet been reduced to a systematic form, is now presented to the Student, particularly in the chapters on *Adhesion*, on *Heat*, and on *Voltaic Electricity*.

It is proposed to complete the work in Three Parts. The Second Part, which will be devoted to *Inorganic Chemistry*, is expected to be ready by the end of the present year; and the Third Part, which will embrace *Organic Chemistry*, in the spring of next year.

As the Author was originally a pupil of Professor Daniell, and was subsequently, for several years, associated with him as Lecturer on Chemistry, it has happened that, in some of the subjects treated of in this volume, the

thoughts and mode of arrangement resemble those adopted by that distinguished philosopher in his *Introduction to the Study of Chemical Philosophy.*

The second Edition of that work was published so far back as 1843; and even if the work itself had not been long out of print, the progress of science would have detracted greatly from its utility as a text-book. The adaptation of that work to the systematic teaching of the present day would have involved changes of an extensive character: moreover, every teacher who takes an interest in the progress of his class has his own views and methods. The Author, therefore, judged it better, after much consideration, to bring out a new work, leaving untouched that of his late Master as the true exponent of his views upon some of those branches of science which his researches had contributed to advance and adorn.

The Author cannot omit to avail himself of the present opportunity of expressing his obligations to his friend, Mr. C. Tomlinson, for many valuable suggestions, and for the warm interest which he has taken in the progress of the work, but more especially for the devotion of no inconsiderable portion of time and labour to the revision of the proof-sheets.

King's College, London, March, 1855.

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Aluminium . .	Al	27·5	Mercury . . .	Hg	200
Antimony . .	Sb	122	Molybdenum .	Mo	96
Arsenic . . .	As	75	Nickel . . .	Ni	59
Barium . . .	Ba	137	Niobium . . .	Nb	94
Bismuth . . .	Bi	210	Nitrogen . . .	N	14
Boron	B	11	Osmium . . .	Os	199
Bromine . . .	Br	80	Oxygen . . .	O	16
Cadmium . .	Cd	112	Palladium . .	Pd	106·5
Cæsium . . .	Cs	133	Phosphorus . .	P	31
Calcium . . .	Ca	40	Platinum. . .	Pt	197·1
Carbon . . .	C	12	Potassium . .	K	39·1
Cerium . . .	Ce	92	Rhodium. . .	Ro	104·3
Chlorine . . .	Cl	35·5	Rubidium . .	Rb	85·4
Chromium . .	Cr	52·5	Ruthenium . .	Ru	104·2
Cobalt. . . .	Co	59	Selenium . .	Se	79·5
Copper . . .	Cu	63·4	Silicon . . .	Si	28
Didymium . .	Di	96	Silver	Ag	108
Erbium . . .	E	112·6	Sodium . . .	Na	23
Fluorine . . .	F	19	Strontium . .	Sr	87·6
Gallium . . .	Ga		Sulphur . . .	S	32
Glucinum . .	G	9·3	Tantalum . .	Ta	182
Gold	Au	196·6	Tellurium . .	Te	129
Hydrogen . .	H	1	Thallium. . .	Tl	203·6
Indium . . .	In	113·4	Thorinum . .	Th	115·7
Iodine . . .	I	127	Tin	Sn	118
Iridium . . .	Ir	198	Titanium. . .	Ti	50
Iron	Fe	56	Tungsten. . .	W	184
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ELEMENTS OF CHEMISTRY.

PART I.

CHEMICAL PHYSICS.

CHAPTER I.

PRELIMINARY VIEW OF CHEMICAL ATTRACTION—LAWS OF COMBINATION.—CHEMICAL SYMBOLS.

(1) *Chemical Distinction of Bodies into Elements and Compounds.*—Modern science has shown that, numberless as are the substances presented to us in the daily experience of life, there are very few which cannot be separated into other substances of a less complicated nature. For example, a piece of wood, a sheet of paper, and a quill pen can each be separated into three or four distinct substances; namely—oxygen, hydrogen, carbon, and nitrogen; but from these we cannot extract any simpler forms of matter. It is the province of chemistry, 1. To resolve matter into its simplest components; 2. To ascertain the properties of these simple or elementary forms of matter; 3. To combine two or more of these elementary bodies with each other, so as to form compounds; 4. To study the properties of these compounds; and 5. To define the conditions under which such compounds can exist.

Bodies which have hitherto resisted all attempts to resolve them into other forms of matter are in chemical language termed *elements*, or *simple substances*. In popular language, the word element is often referred to *fire*, *air*, *earth*, and *water*. A very slight acquaintance with chemistry is sufficient to prove that air, earth, and water are compound bodies, and that fire is mainly the result of the action of a high temperature on certain bodies.

All natural objects then, consist either of simple bodies, or they are composed of two or more simple bodies united according to certain rules or laws which form the groundwork of the science of chemistry. Substances thus produced by the union of two or

more elements are termed *compound* bodies. These compounds have in general no more resemblance in properties to the elements which have united to form them, than a word has to the letters of which it is made up.

Simple or elementary substances are limited in number. In the present state of the science only sixty-four are known. Many of these are widely distributed, and form in mixture or in combination with others, considerable portions of the earth's crust; others have hitherto been found only in minute quantities. Of these simple substances the larger proportion are metals, many of which are familiar to us, such as gold, silver, copper, iron, lead, tin, and mercury. Other simple substances equally familiar have no resemblance to the metals; such as charcoal, sulphur, and phosphorus. Some simple substances exist in the form of air or gas: such, for example, are the two essential components of the atmosphere, oxygen and nitrogen.

Simple substances have been divided into two great classes—*non-metallic** and *metallic*. The substances comprised in the latter class are the more numerous, but those in the former are the more abundant and the most widely distributed.

The elements enumerated as non-metallic are thirteen in number†—viz.,

Oxygen	Chlorine	Sulphur	Boron
Hydrogen	Bromine	Selenium	Silicon
Nitrogen	Iodine	Phosphorus	
Carbon	Fluorine		

Of these substances, oxygen, hydrogen, nitrogen, chlorine, and probably fluorine, are gaseous; bromine is liquid, and carbon, iodine, sulphur, selenium, tellurium, phosphorus, boron, and silicon, are solid at ordinary temperatures.

(2) *Difference between Physical and Chemical Properties.*—The properties which characterize objects in general, may be classed under two heads—viz., *physical* and *chemical*.

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* Some writers speak of the non-metallic bodies as the *metalloids*, a term which signifies metal-like substances. This unfortunate misnomer could never have become even partially current, but for the want of a good single word for the phrase 'non-metallic body.'

† Tellurium is sometimes enumerated among the non-metals, but it more nearly approaches the metals in many of its characters. It possesses a tin white colour and brilliant metallic lustre; its specific gravity is more than 6, whilst that of the heaviest of the non-metals, iodine, is not quite 5. On the other hand, its power of conducting electricity is very low, and it has very great chemical analogies with sulphur and selenium.

The physical properties of an object are those which refer to its condition, whether solid, liquid, or gaseous. Crystalline form, density, hardness, colour, transparency, or opacity, and the relations of the object to heat and electricity are also physical properties. The physical properties of a body have no reference to its elementary composition. The chemical properties of the body, on the contrary, relate essentially to its action upon other bodies, and to the permanent changes in composition which it either experiences in itself, or which it effects upon them. For example, in indicating the physical properties of sulphur, we refer to its brittleness, its crystalline structure, its fusibility and volatility, its faint peculiar odour, its yellow colour, its semi-transparency, its electrical excitability, or the facility with which if rubbed it exhibits electrical attraction, and so on. But in describing the chemical properties of sulphur we indicate its inflammability, its tendency to unite with silver or copper when heated with it, its insolubility in water and alcohol, its solubility in oil of turpentine and in alkaline liquids. In short we notice those operations by which the body usually becomes changed, and loses its distinctive physical characters.

It is not however always possible to draw the line between physics and chemistry; this is of the less importance, since the chemical nature of any substance could be but imperfectly studied, without a tolerably complete knowledge of its leading physical characters, by which it is most readily defined.

(3) *Physical States of Matter.*—Natural objects are presented to us in three states, or physical conditions—viz., the *solid,* the *liquid,* and the *gaseous, aëriform,* or *vaporous.* Every substance exists in one or other of these conditions. The same body may, however, often be made to assume any one of these conditions at different times, and pass from one to the other for an indefinite number of times, according as it is exposed to a greater or less degree of heat. Ice, water, and steam are the same material in three different states. In whatever form matter exists,—whether visible, as in the state of ice or water, or invisible, as in that of steam,—the quantity of matter always remains the same; there can be no destruction of matter. A quantity of ice or of water that weighs a pound, will still, as steam, be equally a pound. So it is with all gases; the air, although invisible, is not the less capable of being weighed and measured.

(4) *Porosity.*—Natural objects, of whatever form, are composed of particles which are not in actual contact, but are separated by spaces or intervals termed *pores.* A lump of sugar or of

salt is at once seen to consist of a collection of smaller solid particles, with intervening spaces; but the porosity of such bodies as water, spirits of wine, or iron, is not so obvious, although the existence of the property is not less certain. The porosity of spirit and of water may be shown as follows:—

Fig. 1.

Take a long narrow tube with a couple of bulbs blown in it, and furnished with an accurately fitting stopper, as represented in fig. 1; fill the tube and lower bulb with water, then carefully and completely fill up the upper bulb and neck with spirit of wine, and insert the stopper. The structure of the apparatus, and the different densities of the two liquids, prevent them from mixing; but on turning the tube upside down and back again three or four times, so as to mix the spirit and the water thoroughly, and then holding the instrument with the bulbs downwards, an empty space will be seen in the tube after they have been thus mixed, showing that they now occupy less space than before; that their particles are in fact closer together. Proofs of porosity are afforded even by the metals; for example, many of them become more compact by hammering, as is the case with platinum; and all of them, not excepting platinum and gold, two of the densest forms of matter, however cold they may be, shrink into a smaller space when rendered still colder. The ultimate particles therefore cannot be in contact.

(4 *a*) *Divisibility of Matter.*—We have no means of determining the real size of the ultimate particles of matter, although, as will be seen hereafter, there are strong grounds for believing that the divisibility of matter, extreme as it is, has its assigned and definite limits. Experience, however, shows that whatever be the form of matter selected for experiment, its divisibility may be manifested to an extent which indicates further divisibility beyond our powers of conception. In the ordinary process of making gold leaf, for example, the gold is hammered out so thin that 280,000 leaves would be required to make up the thickness of an inch, and a single grain of gold is hammered out until it covers a square space seven inches in the side. Each square inch of this may be cut into 100 strips, and each strip into 100 pieces, each of which is distinctly visible to the unaided eye. A single grain of gold may thus, by mechanical means, be subdivided into $49 \times 100 \times 100 = 490{,}000$ visible pieces. But this is not all; if attached to a piece of glass, this gold leaf may be subdivided still further; 10,000 parallel lines may be ruled in

the space of one single inch, so that a square inch of gold leaf, weighing $\frac{1}{4\,9}$ of a grain, may be cut into 10,000 times 10,000, or 100,000,000 pieces, or an entire grain into 4,900,000,000 fragments—each of which is visible by means of the microscope. Yet we are quite sure that we have not even approached the possible limits of subdivision, because, in coating silver wire, the covering of gold is far thinner than the gold leaf originally attached to it, since in drawing down the gilt wire the gold continues to become thinner and thinner each time, in proportion as the silver wire itself is reduced in thickness.

When a substance is dissolved in any liquid, the subdivision is carried still further, and the particles are rendered so minute as to escape our eyesight even when aided by the most powerful magnifiers.

(5) *Varieties of Attraction.*—Mere mechanical subdivision, or even the more perfect separation of the particles of a compound body, by the process of solution, does not put us in possession of the simple substances from which the compound is formed. A piece of loaf-sugar may be reduced, by trituration, to an impalpable powder, but every particle of that powder will still be sugar; it may be dissolved in water, but each drop of the liquid will still contain sugar, unaltered except in appearance. Sugar is composed of three elements—carbon, hydrogen, and oxygen; but trituration or solution in water will not enable us to extract any of these substances from it. The *molecule,* or minutest particle of sugar which can exist, is still a compound body, and still contains its constituent carbon, hydrogen, and oxygen.

The existence of a body as a solid in one continuous mass is owing to *cohesion*—an attraction of considerable intensity, but which varies in degree in different bodies, and by this variation produces varieties in the toughness, hardness, and brittleness of bodies. But the cause which unites the various chemical elements—such as the carbon, hydrogen, and oxygen of sugar—to form a new compound, endowed with properties entirely different from those of any of its constituents, is of a different nature from cohesion, and of a more subtle kind. *Chemical attraction* (or *affinity,* as it is often, but not very philosophically termed) is the cause which unites the elements into compound bodies. It is exerted between the smallest or ultimate particles of one element, and the corresponding particles of the other elements with which it is associated in the particular compound under examination. These ultimate particles are often spoken of as *Atoms,* a term derived from the Greek ἄτομος, 'indivisible,' which

implies that the particles admit of no further subdivision. We may, in fact, contrast the effects of chemical attraction with those of cohesion, by stating that the molecule of a body is formed by the union of atoms under the influence of chemical attraction, whilst the mass is formed by the union of molecules under the influence of cohesion.

The separation of a body into its constituents is the business of *chemical analysis* (from *ἀνα*, 'up,' or 'backwards,' and *λύσις*, 'separation'), and it has for its object, first, the determination of the *nature* of the components—this is *qualitative* analysis; secondly, the determination of their *quantity*—this being *quantitative* analysis. The successful performance of these operations of analysis requires an extensive acquaintance with the principles and the facts of the science, combined with considerable skill in manipulation, or the management of chemical apparatus and processes.

On the other hand, chemical *synthesis* (from *σὺν*, 'together,' *θέσις*, 'putting'), the production of new compounds by the union of their elements, is an operation the reverse of analysis, and constitutes another equally important portion of the labours of the chemist.

(6) *General Characters of Acids, Alkalies, and Salts.*—It will assist the comprehension of our remarks on chemical attraction if we allude briefly to the general characters of three very important classes of compounds—viz., *acids, alkalies,* and *salts.*

The term *acid* was originally applied to certain substances which are soluble in water, have a sour taste, and exert such an action on vegetable blue colours as to change them to red. For example, tincture of litmus, which is of a blue colour, is exceedingly sensitive to the action of an acid: paper stained with this tincture is in frequent use by the chemist for detecting the presence of acids.

The term *alkali* is of Arabic origin: it was given in the first instance to carbonate of soda, or sodic carbonate, which was then obtained from the ashes of sea-weeds; but it is now extended to a class of substances possessing many qualities exactly the reverse of those which belong to the acids. An alkali is soluble in water, and produces a liquid soapy to the touch, and of a peculiar, nauseous taste; it restores the blue colour to vegetable infusions which have been reddened by an acid; it turns many of these blue colours into green, as in the cases of the solutions of red cabbage and of syrup of violets; and it gives a brown colour to vegetable yellows, such as those of turmeric and rhubarb. Litmus paper

which has been feebly reddened by an acid affords a ready test of the presence of an alkali, and is more sensitive than paper stained with turmeric or with rhubarb, which is also in common use for the same purpose. These different *test papers,* as they are called, show whether an acid or an alkali predominates in a solution.

Vinegar or acetic acid, oil of vitriol or sulphuric acid, muriatic or hydrochloric acid, aquafortis or nitric acid, are familiar instances of the class of acids. Potash, soda, and hartshorn or ammonia, are instances of well-known alkalies.

Many of the acids and all the alkalies are remarkable for their great chemical activity. Nitric acid attacks copper quickly and violently, with brisk effervescence, and the copious escape of red fumes, whilst a blue liquid is formed from the action. Sulphuric acid shows similar energy, if mixed with water and placed in contact with iron or zinc. Moreover, both these acids, when not much diluted with water, produce speedy destruction of the texture of nearly all animal and vegetable matters. The solvent action of potash, or of soda, is not less marked. Either of these alkalies destroys the skin if allowed to remain upon it; and also gradually dissolves portions of earthenware, or of glaze from the vessels which contain it, and the solution, if suffered to fall upon a painted surface, quickly removes the paint. But the most remarkable property of acids and alkalies is the power which they have of acting upon each other, and destroying or *neutralizing* the chemical activity which distinguishes them when separate.

Some of these properties of acids and alkalies may be submitted to experiment by means of a coloured vegetable solution, such, for example, as the purplish liquid prepared by slicing a red cabbage and boiling it with water. If a quantity of this infusion be divided into two portions, and to the one be added a quantity of diluted sulphuric acid, a red liquid is obtained; and if to the other a solution of caustic potash be added, a liquid of a green colour is formed: then, on gradually pouring the alkaline into the acid solution, stirring the mixture constantly, the green colour of the portions first added instantly disappears, and the whole liquid remains red; as more and more of the alkali is added, the red passes by degrees into purple, and on continuing to add the alkaline solution, a point is attained when the liquid has a clear blue tint: at this moment there is neither potash nor sulphuric acid in excess in the liquid, the two having chemically acted upon one another, and the characteristic properties of both have disappeared. On evaporating the solution at a gentle heat, a solid

crystalline substance, resulting from the chemical action of the sulphuric acid upon the potash, is obtained. This substance is the salt called *sulphate of potash,* or *potassic sulphate.* For the present it may be sufficient to state, that any compound produced by the action of an acid on an alkali, or rather, that is the result of the action of an acid upon a base, is termed a *salt.* Other modes of forming salts will be mentioned hereafter.

It must not be supposed that all acids closely resemble those which have just been mentioned, and which are freely soluble in water; some acids, like the citric, tartaric, and oxalic, may be readily obtained in crystals: other acids are not at all soluble in water; as, for example, metastannic acid, the white substance obtained by the action of nitric acid upon tin. The leading character of an acid, in a chemical sense, is its power of reacting with alkalies to form salts; and this character is possessed by various bodies not familiarly regarded as acids. Of course if an acid be insoluble, it has no sourness, and is without action on vegetable blues.*

There are no insoluble alkalies, but there are substances

* Most chemists, following Gerhardt's practice of limiting the title of acid to a particular class of substances which contain hydrogen, now regard all true acids as salts of hydrogen. Formerly many bodies, such as silica or white arsenic, were regarded as acids, though, if we adopt the foregoing definition, they are not really so until they have combined with water. Such bodies, since they contain no hydrogen, are now distinguished as *anhydrides;* the substance familiarly known as *carbonic acid* must, upon this principle, be termed *carbonic anhydride.*

The characters of acids and of salts, and their various modifications, will be more fully discussed hereafter, when the general properties of the metals and of their compounds are considered.

It may, however, be useful in this place to quote the definitions of the terms *acid, base,* and *salt* given by Dr. Frankland in his 'Lecture Notes for Chemical Students':—'An acid may be defined as a compound containing one or more atoms of hydrogen which become displaced by a metal when the latter is presented to the compound in the form of a hydrate. The hydrogen capable of being so displaced may be conveniently termed *displaceable hydrogen.* An acid containing one such atom is said to be monobasic, two such atoms, dibasic, &c. Acids of a greater basicity than unity are frequently termed *polybasic acids.*'

'The term *base* is applied to three classes of compounds, all of which are converted into salts by the action of acids. These are:—1st. Certain compounds of metals with oxygen, such as sodic oxide (Na_2O), zincic oxide (Zn O), &c. 2nd. Certain compounds of metals with the compound radical hydroxyl (HO), such as sodic hydrate (Na (HO)), zincic hydrate ($Zn (HO)_2$), &c. 3rd. Certain compounds of nitrogen, phosphorus, arsenic, and antimony, such as ammonia (NH_3).'

'By the mutual action of an acid and a base upon each other, a *salt* is produced, (see following note).

greatly resembling them which are but sparingly soluble, such as lime and baryta; these are termed *alkaline earths*. There are also numerous other analogous substances, compounds of oxygen with the metals, termed *oxides*, such for instance as the compound of silver with oxygen, or argentic oxide, the compound of iron with oxygen, or ferric oxide, and that of lead with oxygen, or plumbic oxide, which are insoluble in water, but which are easily dissolved by acids, forming on evaporation crystalline compounds or salts. For instance, by the action of nitric acid upon argentic oxide, argentic nitrate and water are produced* (1); with sulphuric acid and ferric oxide, ferric sulphate and water are the products (2); whilst with acetic acid and plumbic oxide, plumbic acetate and water are obtained (3). Any substance, whether soluble in water or not, is called a *base* if it thus have the power of reacting with acids, neutralizing their properties, and furnishing by such action a salt, whilst at the same time water is formed. Hence the alkalies constitute one subdivision of the more numerous class of bodies known as bases.

(7) *Characters of Chemical Attraction.*—Chemical attraction is distinguished by well-marked characters from other kinds of action which take place within minute distances.

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* A metal which by its union with oxygen produces a base is designated as a *basyl*. Argentic oxide, or oxide of silver, for example, is a base, whilst silver itself is a basyl. So also plumbic oxide is a base, whilst lead is regarded as a basyl, when we refer to its occurrence in its salts. In a similar manner water is itself, when compared with acids, sometimes spoken of as a base, whilst hydrogen is a basyl. When a base containing oxygen acts upon an acid, which, as has already been defined, is a salt of hydrogen, the hydrogen in the acid and the metal in the base change places, a metallic salt is formed, and water is set at liberty, as is shown by the following symbols and equations, which illustrate the formation of argentic nitrate, ferric sulphate, and plumbic acetate respectively :—

(1) $Ag_2O + 2\,HNO_3 = H_2O + 2\,AgNO_3$
(2) $Fe_2O_3 + 3\,H_2SO_4 = 3\,H_2O + Fe_2(SO_4)_3$
(3) $PbO + 2\,HC_2H_3O_2 = H_2O + Pb(C_2H_3O_2)_2$.

The explanation of the principle upon which these symbols are constructed will be found at p. 23.

We meet not unfrequently with bases in which hydrogen as well as a basylous metal is present, *e.g.* in caustic soda (Na HO), or slaked lime ($Ca\,H_2O_2$). Salts are also formed by the action of such compounds upon the acids, and at the same time the hydrogen both of the acid and of the base is separated in the form of water. This, for example, is what occurs when hydrated soda is neutralized by hydrochloric acid, common salt and water being the products; for instance :—

$$Na\,HO + HCl = H_2O + Na\,Cl;$$

or when slaked lime is converted into calcic sulphate by sulphuric acid :—

$$Ca\,H_2O_2 + H_2SO_4 = 2H_2O + Ca\,SO_4.$$

i. Chemical attraction is exerted within its own limits with intense energy; but beyond those limits it is entirely powerless. An iron wire, for example, which will support a weight of 1000lb., will in a few minutes yield to the almost noiseless action of a mixture of nitric acid and water; the stubborn metal will be dissolved, and a clear solution of the metallic mass will be formed: the metal will be detached from the wire particle by particle, and no vestige of its structure or tenacity will remain. It is rarely possible, by trituration or other mechanical means, to bring about a sufficient approximation amongst the subdivided particles to produce chemical action. Tartaric acid and sodic carbonate, each in the form of a dry powder, may be incorporated by grinding for hours in a mortar, but they will not act chemically upon each other: it is not until a more intimate contact is effected by the addition of water, which dissolves the particles of both, and allows them mutually to approach closer, that the brisk effervescence, due to the expulsion of the carbonic anhydride, occurs, which indicates the transfer of the sodium with which it was previously in combination, to the radicle of the tartaric acid, and the formation of water and sodic tartrate.

It is important to distinguish clearly between a mere mechanical *mixture* and a chemical *compound*, for the effects produced by mixture and by combination are very different. In a mixture the proportions of the materials may be varied at pleasure, and the properties of the mixture will partake of those of each of its constituents; whereas in a chemical compound the proportion of each of its constituents is invariable, and the properties of the compound are nearly always quite different from those of the bodies which have entered into its formation.

A striking illustration of the difference between the effects of mechanical intermixture and those of chemical combination is afforded in the case of ordinary gunpowder. In the manufacture of this substance, the materials of which it is made—viz., charcoal, sulphur, and nitre—are separately reduced to a state of fine powder; they are then intimately mixed, moistened with water, and thoroughly incorporated by grinding for some hours under edge stones; the resulting mass is subjected to intense pressure, and the cakes so obtained, after being broken up and reduced to grains, furnish the gunpowder of commerce. In this state it is a mechanical mixture of nitre, charcoal, and sulphur. The nitre may be washed out of the mixture by means of water, the sulphur by means of carbonic disulphide, while the charcoal will be left undissolved. By evaporating the water, the nitre may be

obtained; and on allowing the disulphide to volatilize, the sulphur will be left behind. If, however, we cause the materials to act chemically on one another, all is changed:—a spark fires the powder; the dormant chemical attractions are called into operation, the charcoal disappears, a large volume of gaseous matter is liberated, and new substances are produced, which have no resemblance to the original mixture.

ii. Chemical attraction is most strongly exerted between dissimilar substances.* No manifestation of this attraction takes place between two pieces of iron, two pieces of copper, or two pieces of sulphur; but between sulphur and copper, or sulphur and iron, chemical action of the most energetic kind may occur. It is highly probable, however, as will be seen hereafter, that in many cases the isolated bodies usually viewed as elements should be regarded as compounds, the molecules of which consist of particles of the same element in opposite polar or electrical conditions. Hydrogen gas, for instance, is to be regarded as *hydride of hydrogen*, or a compound of hydrogen with hydrogen; chlorine gas, as *chloride of chlorine*, and so on.

Many compound bodies, when subjected to the action of the voltaic current in a liquid state, are decomposed, one of the elements going to the positive electrode of the voltaic battery, the other to the negative electrode. The elements have hence been divided into two groups according to their electrical relations, those which are separated at the positive electrode being termed *electro-negative*, or *chlorous* elements, which include such bodies as chlorine, iodine, oxygen, and sulphur; whilst those which are found at the negative electrode are termed *electro-positive* or *basylous* elements (261), among which are comprised potassium, sodium, and other metals which, when united with oxygen, form bases.

Generally speaking, the greater the difference in the properties of the two bodies, the more intense is their tendency to mutual chemical action. Two electro-positive elements may combine, as may also two electro-negative elements; but such compounds are much less stable than those formed by the union of an electro-positive with an electro-negative element. For instance, the metals, as a class, combine readily with chlorine, oxygen, and

* This circumstance—viz., that the elements which combine are not allied in properties—is sufficient to indicate the objection to the use of the term *affinity*, to express this form of attraction, although custom has sanctioned its employment.

sulphur:—silver unites rapidly with sulphur, iron with chlorine, potassium with oxygen, and so on. But between bodies of a similar character the tendency to unite is feeble. For example, chlorine and oxygen can only be made to combine by indirect methods, and when combined, a slight elevation of temperature is sufficient to cause them to separate from each other. In like manner, two metallic bodies, copper and zinc, will, under the influence of a high temperature, unite and form brass,—an alloy, the properties of which indicate that it may be regarded as a chemical compound; but brass, on being heated strongly, may be separated into zinc, which nearly all passes off in vapour, and copper, which is left behind.

Even in bodies of the same class chemical attraction is exerted between different kinds of matter with different but definite degrees of force. Nitric acid will dissolve most of the metals—such, for instance, as silver, mercury, copper, and lead—and by so doing will produce a nitrate of each metal; but the chemical compounds thus formed are held together with very different degrees of energy. The combination with silver at ordinary temperatures is less powerful than with mercury, less so with mercury than with copper, and with copper less again than with lead.

This fact may easily be determined by dissolving half an ounce of argentic nitrate (nitrate of silver) in half a pint of water, and pouring into it a small quantity of clean mercury; in the course of a few days a beautiful crystallization of metallic silver will be obtained, whilst a corresponding quantity of mercury will be dissolved, and will combine with the nitrion (NO_3) previously in union with the silver. In a similar manner mercury may be displaced from a solution of mercurous nitrate by means of a strip of metallic copper; and copper, in its turn, may be displaced by a piece of lead introduced into a solution of cupric nitrate. From a solution of plumbic nitrate, zinc will, in like manner, displace the lead, which will be deposited in beautiful crystals.

Guided by facts like these, different elements have been arranged in tables indicating the order of their attraction for any one element which is placed at the head of the list. For example, in the first column of the following table, several of the more important metals are arranged in the order of their tendency to combine with oxygen,—the metal at the head of the list having the strongest attraction for that element, that which stands second the next, and so on to the one mentioned last, in which the attraction is the weakest:—

Order of Displacement from Solution.

OXYGEN.	SULPHURIC ACID.
Potassium.	Baryta.
Zinc.	Potash.
Tin.	Soda.
Lead.	Lime.
Copper.	Ammonia.
Mercury.	Zincic oxide.
Silver.	
Gold.	

Similar tables may be formed, exhibiting the relative tendency of compound bodies, such as bases, to displace each other from the salts which they have contributed to form. In the second column of the table, the various bases are arranged in the order in which they displace each other at ordinary temperatures from the salts which they form when acted on by sulphuric acid.

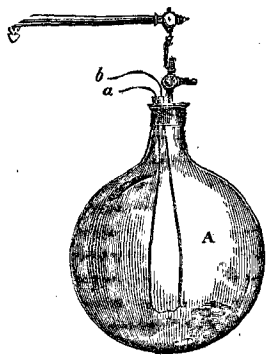
iii. Another of the most remarkable and characteristic features of chemical attraction is the entire change of properties which it occasions in both the substances dealt with,—a change which no *à priori* reasoning could possibly have predicted. If the blue liquid obtained by dissolving copper in nitric acid be evaporated, there will be formed a blue crystalline salt which has none of the chemical properties either of the acid or of the metal from which it was procured. There is an equally striking difference between the tough, metallic, insoluble iron, and the corrosive oil of vitriol, and the beautiful crystalline, green, soluble, inky-tasted salt which is produced by their mutual action.

iv. The experiments on the displacement of one metal by another, further show that although in combination, the properties of the components are masked, and to all ordinary observation the constituents have disappeared, whilst new bodies have been formed, yet these component elements do really exist in the compound, and can be again reproduced in their original form by separating them from each other.

It is, indeed, a general principle, that whenever chemical combination occurs, there is no destruction of matter. However much the materials may change their form, the weight of the new products, if collected and examined, will be found to be exactly equal to that of the substances before combination. The following experiment shows that, even although the substance may vanish from our sight, it continues to exist as a gas, which has the same weight

as the solid which furnished it:—Into a glass flask *A* (fig. 2), of the capacity of about 250 cubic inches, or 4 litres, and which is provided with a brass cap and stop-cock, introduce 10 or 12 grains (0·6 or 0·7 gramme) of gun-cotton; attach the flask to the air-pump, exhaust it completely, and afterwards weigh it. Then set fire to the cotton by means of a voltaic current sent through the wires, *a, b,* which are insulated from each other and from the cap of the instrument, by passing through a varnished cork. The cotton will entirely disappear with a brilliant flash, but the flask, if weighed again, will be found to be of the same weight as it was before the cotton was fired.

FIG. 2.



v. There are two modes of forming chemical compounds; the simplest is that in which the two substances unite directly together, as when hydrogen burns in air, and, by direct union with oxygen, produces water; or when an acid and an alkali, such as hydrochloric acid and ammonia, combine and produce a salt. This mode of combination usually prevails between bodies which have a powerful tendency to unite. The other mode is still more common: it occurs when one of the ingredients of a compound is displaced by another substance, and a new compound is the result. The instances already specified, in which one metal precipitates another from its solution, are cases in which new bodies are produced by the displacement of one of the substances in a compound previously formed. This method of forming compounds by displacement, or *substitution,* is one of great importance; and the study of its various modes of action is rapidly contributing to the discovery of many subtle processes concerned in the chemistry of organized beings.

vi. Chemical combination, in a large proportion of cases, does not commence spontaneously. A heap of charcoal may remain unaltered in the air for years; but, if a few fragments of it be made red hot, chemical action will begin at the spot to which the heat is applied, and it will continue until the whole mass is burned; that is, the chemical action between the oxygen of the air and the charcoal will continue as long as any charcoal is left. In other instances, however, the chemical effects begin more readily. A piece of phosphorus begins to be oxidized slowly the instant it comes into the atmosphere, and in warm weather it

often bursts into a blaze. Again zinc ethyl, a liquid containing zinc, carbon, and hydrogen, inflames on being brought in contact with the air at ordinary temperatures, though at low temperatures oxidation takes place less rapidly and without inflammation. In all these cases, therefore, heat is necessary to start the action; the difference being one of degree and not of kind.

vii. Whenever substances unite directly with each other, heat is emitted, and the more rapidly the union is effected, the larger is the quantity of heat emitted in a given time, until, in some cases, it rises so high as to produce ignition and combustion; light and heat are abundantly evolved when the temperature rises high enough, since all substances, when heated beyond a certain point, become luminous.

When compounds are formed by substitution, the liberation of heat is usually much less, and is sometimes not perceptible without special contrivances.

viii. The physical state of one or of both the bodies which enter into combination is frequently altered by the operation of chemical attraction. Two solids may become converted into a liquid; two liquids, or even two gases, may become solid. Differences of state are therefore not in all cases due to differences of temperature; differences in the chemical arrangement of the particles are equally important in bringing about physical differences of condition.

The foregoing leading characters, by which chemical attraction is distinguished from other sources, may be thus summed up:—

Chemical attraction is an action of extreme energy, which acts only on the minutest particles of matter, and at distances too small to be perceptible. Under its influence the elementary bodies, though comparatively few in number, arrange themselves into the numberless compounds which constitute the different forms of matter in the three great kingdoms of nature; and it is important to observe that the proportions in which they unite are fixed and invariable. Chemical attraction operates between the particles of dissimilar kinds of matter and by its exertion produces new properties in the resulting compound. It exists between different kinds of matter with different but definite degrees of intensity. As a result of its operations, no destruction of matter occurs in the materials submitted to its influence; there is consequently no loss of weight, but only change of form. The act of combination may either occur instantly on mixture, or it may be indefinitely postponed till some other action, such as heat, con-

curs to commence the change. Compounds may be formed either by the direct union of their ingredients, or by the displacement of one substance by a different one in a compound previously formed; and lastly, heat and light, in amount proportioned to the rapidity of the action, are generally emitted in cases of the direct union of the constituents.

(8) *Laws of Combination.*—The relative proportion in which the different elements unite is regulated by fixed laws. These laws, which form the basis of chemical science, are three in number, and they regulate the mode of combination of every known chemical compound. They are usually termed the *laws of chemical combination.*

(9) The first of these laws, the law of *Definite Proportions,* may be stated in very few words; it is as follows:—*In every chemical compound the nature and the proportions of the constituent elements are definite and invariable.* For instance, 100 parts of water contain 88·9 of oxygen and 11·1 of hydrogen, or the weight of the oxygen is always exactly eight times that of the hydrogen. Whether water be derived from the snows of high mountains, from rain clouds, from dew, or from direct chemical action, as when the hydrogen of a burning lamp or candle unites with the oxygen of the air, its composition is uniform and certain. So also a piece of flint, or of rock crystal, in whatever part of the world it be found, will, on analysis, yield in every 100 parts 46·7 of silicon and 53·3 of oxygen. So also hydrochloric acid gas, however obtained, always contains in 100 parts 97·26 of chlorine and 2·74 of hydrogen. In fact, experiment shows that all true chemical compounds which have been submitted to analysis have a composition equally definite. It is this law of definite proportions which gives value to analysis, by affording certainty and uniformity to its results. Mere mechanical intermixture is at once distinguished from true chemical combination by the absence of all regularity in the proportions of the bodies that have been mingled: and in the same manner chemical attraction stands strongly contrasted with that kind of adhesion which produces the solution of solids in a liquid, or the intermixture of two liquids like spirit of wine and water with each other.

(10) The second law of combination is the law of *Multiple Proportions.* It frequently happens that the same pair of elementary bodies unites together in more than one proportion. The compounds so obtained are usually very different from each other; but there is always a regularity in the plan upon which these

compounds are formed, and the ratios of the two elements in each are very simply related. This law may be thus stated:—*When two elements, A and B, unite together in more ratios than one, if we compare together quantities of each of the resulting compounds which contains the same amount of A, the quantities of B will bear a very simple relation to each other;* such as

$$A+B,\quad A+3B,\quad A+5B,\ \&c.;$$
$$\text{or,}\quad A+2B,\quad A+4B,\quad A+6B,\ \&c.$$
$$\text{or,}\quad 2A+3B,\quad 2A+5B,\quad 2A+7B,\ \&c.;$$

Water, for instance, is a compound of oxygen and hydrogen; in 100 parts there are, as already mentioned, 88·9 of oxygen and 11·1 of hydrogen. But there is another compound of oxygen and hydrogen known to chemists, termed hydric peroxide, or hydroxyl. By analysis it has been found that 100 parts of this body contain 94·1 of oxygen and 5·9 of hydrogen. Now, on comparing together the quantities of oxygen which in these two compounds are united with an equal quantity, say 2 grammes of hydrogen, it is evident that in water, for 2 grms. of hydrogen there are 16 of oxygen,

$$\text{since } 11{\cdot}1 \;:\; 88{\cdot}9 \;::\; 2 \;:\; 16$$

and by a similar process it is seen that in hydric peroxide, for 2 grms. of hydrogen 32 grms. (or 16×2) of oxygen are present:—

$$5{\cdot}9 \;:\; 94{\cdot}1 \;::\; 2 \;:\; 32$$

the quantity of oxygen combined with the hydrogen in the peroxide being just double of that combined with the same quantity of hydrogen in water.

Mercury in like manner forms two compounds with chlorine—viz., calomel, and corrosive sublimate. In calomel 200 grammes of mercury are combined with 35·5 of chlorine; whilst in corrosive sublimate the 200 of mercury are united with 71 grammes of chlorine, or with just twice as much.

A similar simple ratio between the quantities of the combining elements is found to hold good in every series of compounds formed by the union of two elements with each other. A certain quantity of one of the elements combines with a certain quantity of the other: in the next compound with twice as much as in the first; in the next with three times as much; in the next with four times as much, and so on.

An excellent example of this regularity is afforded by the series of compounds which nitrogen forms with oxygen. They are

five in number, and contain in 100 parts of each, the following ratio of their constituents, the oxygen increasing in amount from the first to the fifth :—

	Oxygen.	Nitrogen.
Nitrous oxide	36·36 ...	63·64
Nitric oxide	53·33 ...	46·67
Nitrous anhydride	63·16 ...	36·84
Peroxide of nitrogen . . .	69·57 ...	30·43
Nitric anhydride	74·07 ...	25·93

Now on comparing quantities of each of these different compounds which contain equal quantities of nitrogen, and in the order in which the compounds stand in the foregoing table, it will be seen that the oxygen increases in quantity in the proportion of 1, 2, 3, 4, and 5. In the nitrous oxide the quantity of nitrogen combined with 16 parts of oxygen is 28, and taking this amount of nitrogen in each case, we obtain by proportion the following series :—

Oxygen.		Nitrogen.				
36·36	:	63·64	: :	16	:	28
53·33	:	46·67	: :	32 (16 × 2)	:	28
63·16	:	36·84	: :	48 (16 × 3)	:	28
69·57	:	30·43	: :	64 (16 × 4)	:	28
74·07	:	25·93	: :	80 (16 × 5)	:	28

the quantity of the oxygen increasing progressively, in the proportion of 16, twice 16, 3 times 16, 4 times 16, and 5 times 16.

In some cases the ratio in which the elements unite is rather less simple, two parts of one element combining with 3, 5, or 7 of the other.

This important law was first clearly established by Dalton.

(11) The third law of combination is usually known as the *Law of Equivalent Proportions*. It may be stated as follows:— *Each elementary substance, in combining with other elements, or in displacing others from their combinations, does so in a fixed ratio, which may be represented numerically.*

This principle of equivalent ratio may be illustrated by reference to the experiments upon the displacement of the metals from solutions of their nitrates (p. 12), or still more simply from solutions of their chlorides, by the introduction of some other metal, the attraction of which for the chlorine is stronger than that of the metal with which it is already combined. When, for instance, a slip of copper is introduced into a solution of mercuric chloride, the two metals change places, owing to the stronger

chemical attraction of the chlorine for the copper than for the mercury; a portion of the copper is dissolved, cupric chloride is formed, and a corresponding quantity of mercury is deposited. On making the experiment with suitable care, it is found that for each 31·74 milligrammes of copper dissolved, 100 of mercury are separated in globules. In a similar way, when a strip of zinc is placed in a solution of cupric chloride, a deposit of metallic copper is separated, and for every 31·74 mgrms. of copper thrown down, the zinc will lose 32·5 mgrms. in weight, whilst a corresponding amount of zincic chloride is formed in the liquid. Finally, if into a solution of hydrochloric acid a rod of zinc be introduced, hydrogen will be set free; and if the volume of the gas be measured, it will be found that 1 mgrm. of hydrogen is liberated for every 32·5 mgrms. of zinc dissolved.

From this series of experiments we learn that different but definite amounts of the various metals are capable of displacing each other; for it appears that 100 parts of mercury, 31·74 of copper, 32·5 of zinc, and 1 of hydrogen, are each capable of exactly supplying the place of the other, in combination with one uniform amount (35·5 parts) of chlorine; and these different quantities of the metals are said to be chemically *equivalent* to each other, and the numbers obtained in this way form the *combining ratios* of the different elements. For the purpose of conveniently comparing together the quantities of the different elements which are thus equivalent to each other, it is necessary to select one element as the unit or standard of comparison. With this view chemists have agreed to take *hydrogen as their unit* or starting-point, since it is the element which enters into combination with a smaller equivalent part than any other. It must not, however, be supposed that the equivalent quantities of the elements can usually be ascertained by direct substitution for a given quantity of hydrogen: recourse is had therefore to indirect processes, such as the determination of the ratio in which each element unites with a fixed quantity of some other element, such as chlorine or oxygen. It is important to distinguish between the ideas *chemical equivalent* and *combining proportion*, or more correctly, *combining ratio*. Bodies can only be said to be equivalent to each other when they can be substituted for each other in combination, and form compounds more or less analogous; the proportion in which they thus displace each other, constitutes their equivalent proportion or numerical chemical equivalent. Definite quantities of silver, copper, iron, zinc, and potassium, for example, may be substituted one for the other in combination

with a given quantity of chlorine. In like manner, certain quantities of chlorine, of bromine, and of iodine, may be made to combine with a given quantity of silver; the quantity of bromine which will displace the iodine, or that of chlorine which will displace the bromine, being the true equivalent quantities of these elements, when compared with each other. It must not be supposed that this equivalence implies any equivalence of chemical energy of the different elements. This energy may be, to some extent, measured by the quantity of heat evolved during the combination of the elements with one another, and this is by no means the same when equivalents of different elements are employed (199 *et seq.*). But if we compare a certain quantity of chlorine with a quantity of potassic chloride which contains an equal quantity of chlorine (inasmuch as chlorine and potassic chloride cannot be substituted one for the other in any compound), the number which represents that ratio in which the two elements have united to form potassic chloride cannot, *as compared with the standard quantity of chlorine,* properly be called its equivalent, but only its *combining proportion,* or *combining ratio.*

(12) *Tables of Equivalent Numbers.*—Chemists are in the habit of referring the results obtained by analysis to the quantity contained in 100 parts of the body submitted to experiment. For instance, it has been ascertained by analysis that 100 parts of hydrochloric acid contain 97·26 of chlorine, and 2·74 of hydrogen; that 100 parts of zincic chloride contain 52·21 of chlorine, and 47·79 of zinc; that 100 of cupric chloride contain 52·80 of chlorine, and 47·20 of copper; that 100 of mercuric chloride contain 26·20 of chlorine, and 73·80 of mercury; and that 100 of argentic chloride contain 24·74 of chlorine, and 75·26 of silver. These illustrations are sufficient to prove that the quantity of chlorine is not the same in the compounds which it forms with the several elements; but this method of stating the result is not adapted to exhibit the numerical relations of these quantities in their simplest form. These relations are rendered much more evident in the following way. Having ascertained the quantity of each constituent in 100 parts of the various compounds which each elementary body forms when it combines with chlorine, let us determine by calculation that ratio in which each element unites with the same *fixed quantity of chlorine,* and let us take for our fixed quantity of chlorine the quantity of it which enters into combination with 1 part (say 1 gramme) of hydrogen. This is easily calculated, since we know that 100 parts of hydrochloric

acid contain 97·26 of chlorine, and 2·74 of hydrogen; consequently

2·74 : 97·26 :: 1 : 35·5

or 35·5 grms. of chlorine are united in hydrochloric acid with 1 grm. of hydrogen. Now, it is easy to ascertain, by similar calculations, the quantity of each of the elements enumerated in the foregoing series of chlorides which is combined with 35·5 grms. of chlorine.

In zincic chloride, for example, 32·5 grms. of zinc are united with 35·5 of chlorine; for

52·21 : 47·79 :: 35·5 : 32·5

In cupric chloride 35·5 of chlorine are united with 31·74 grms. of copper; for

52·8 : 47·2 :: 35·5 : 31·74

In mercuric chloride 35·5 grms. of chlorine are united with 100 of mercury; for

26·2 : 73·8 :: 35·5 : 100

whilst in argentic chloride 35·5 of chlorine are united with 108 grms. of silver; since

24·74 : 75·26 :: 35·5 : 108

consequently one part of hydrogen, 32·5 parts of zinc, 31·74 of copper, 100 of mercury, and 108 of silver are chemically equivalent to each other, since they each combine with the same quantity (35·5 parts) of chlorine.

But results, when obtained by experiments conducted on this plan, are not always free from ambiguity, for there are cases in which the same metal appears to have more than one equivalent number. Mercury, for example, forms another chloride, calomel, which is quite different from the one above described; it contains twice the quantity of mercury combined with our standard quantity of chlorine, or 200 grms. of mercury with 35·5 of chlorine. In like manner copper forms another chloride, which contains twice as much copper as the one above described, or 63·4 grms. of copper combined with 35·5 grms. of chlorine.

Which of these two proportions of mercury or of copper is to be taken as the equivalent of the metal? Each of the two numbers thus obtained is in fact the true equivalent under the particular circumstances; so that both mercury and copper have two equivalents; and the same thing is true of iron, of tin, of plati-

num, and of several other elements. The ambiguity thus occasioned may, however, be removed by means of a conception known as the atomic hypothesis, first distinctly enunciated by Dalton, though it has since been in some degree modified.

(12 *a*) *Hypothesis of the Atomic Constitution of Matter.*—Dalton's atomic theory is that every element is composed of ultimate particles or *atoms*, which cannot be further subdivided by chemical or mechanical means. That these atoms are, in the same element, exactly equal in size and in weight, and absolutely similar in all respects. That the atoms of any one element differ from those of all the other elements in mass and in chemical properties. And that whenever combination takes place between any two elements, union occurs between them atom to atom. If these assumptions be admitted, we find—

1°. That the ratio in which combination occurs must, when the same compound is formed, always be *definite;* since that ratio is determined by the relative weights of the atoms of the combining elements, and the atom cannot be subdivided.

2°. That when the same elements unite in several ratios, these ratios must vary according to the terms of a *simple series of multiples,* since each atom of one element must unite with the other element in the ratio of 1, of 2, or of 3 atoms, or in some other ratio almost equally simple, inasmuch as the atom does not admit of subdivision.

3°. That combination must occur also in *equivalent* proportion; since the equivalent amounts of each element must be in the proportion either of the weights of their atoms, or of a simple multiple of those weights.

In order to elucidate these statements further, let us suppose, for example, that an atom of mercury weighs 200 times as much as the atom of hydrogen, that the atom of silver weighs 108 times as much, the atom of sodium 23 times as much, the atom of chlorine 35·5 times as much, and the atom of oxygen 16 times as much,—it follows that when chlorine and silver unite to form argentic chloride, if one atom of each element enters into each molecule of the compound, this chloride must necessarily and invariably contain, in 143·5 parts, be they grammes, grains, or pounds, 108 of silver, and 35·5 of chlorine.

In like manner, if each of the molecules of sodic chloride be formed by the union of one atom of sodium with one atom of chlorine, then 58·5 parts will necessarily consist of 23 parts of sodium, and 35·5 of chlorine.

So also, if each molecule of water consists of 2 atoms of

hydrogen and 1 atom of oxygen, it must happen that 18 parts of water will always contain 2 parts of hydrogen and 16 of oxygen. Again, if calomel be formed of 1 atom of mercury and 1 of chlorine, it is a matter of necessity that in 235·5 parts of calomel, 200 consist of mercury, and 35·5 of chlorine; while, if corrosive sublimate be formed by the union of 1 atom of mercury with 2 atoms of chlorine, 271 parts of this chloride must contain 200 parts of mercury, and 71 of chlorine, or twice as much chlorine as is found in calomel.

Suppose now that into a solution of corrosive sublimate a slip of copper be introduced: the copper will displace the mercury; and if the weight of the atom of copper be 63·4 times that of the atom of hydrogen, and cupric chloride be formed by the union of 1 atom of copper and 2 atoms of chlorine, the mercury displaced must be in the proportion of 200 parts for every 63·4 parts of copper which enter into solution. In other words, 63·4 parts of copper are chemically equivalent to 200 parts of mercury.

Dalton indeed supposed that the chemical equivalents of the elements always represented the relative weights of their atoms, and hence the term *atomic weight* has often been employed as synonymous with the term *chemical equivalent*. But the ideas involved in the two terms are essentially distinct. There can only be one atomic weight of a simple substance; but as we have seen in the case of mercury and of copper, there may be two chemical equivalents for the same element, and, in some cases, the equivalents may be even more numerous. The atomic weight of a body may coincide with its ordinary chemical equivalent, or it may be a multiple of it. The equivalent number is necessarily a direct experimental result; whilst the number adopted for the atomic weight is arrived at from considerations often somewhat complicated, based partly on the law of gaseous volumes (14), partly on the experimental results upon the specific heat of the bodies under investigation (172), and partly on the isomorphism or similarity in crystalline form of bodies of analogous constitution (83).

The table at pp. 24, 25, contains a list of the elementary bodies at present known to chemists, with the atomic weights ascribed to them by the authorities mentioned, as well as the symbols by which each element is indicated in describing chemical changes.

(13) *Symbolic Notation.*—Before proceeding further, it will be advantageous to describe the principles of notation, as applied to the construction of chemical formulæ. This notation constitutes a kind of short-hand, which materially facilitates the representation

Table of Elementary Bodies, with their Symbols and Atomic Weights.

Names of Elements.	Symbols.	Atomic Weights. H=1.	Atomic Weights. O=100.	Authorities.	Compounds with Oxygen, Chlorine, and other Elements.
ALUMINIUM	Al	27·49	171·81	Dumas	Al_2O_3, alumina; Al_2Cl_6, aluminic chloride
Antimony (Stibium)	Sb	122·0	762·5	Do.	Sb_2O_5, antimonic anhydride; $SbCl_3$, antimonious chloride
Arsenicum	As	75	468·75	Pelouze	As_2O_3, white arsenic; $AsCl_3$, arsenious chloride
Barium	Ba	136·84	855·25	Berzelius (Dumas, 137·02)	BaO, baryta; $BaCl_2$, baric chloride
Bismuth	Bi	210·34	1896·25	Dumas	Bi_2O_3, bismuth oxide; $BiCl_3$, chloride
Boron	B	11	68·75	Deville	B_2O_3, boric anhydride; BCl_3, boric chloride
BROMINE	Br	79·97	499·81	Stas; Marignac	HBr, hydrobromic acid
Cadmium	Cd	112·24	701·4	Dumas	CdO, cadmic oxide; $CdCl_2$, cadmic chloride
Cæsium	Cs	133	831·25	Allen and Johnson	Cs_2O, cæsia; $CsCl$, cæsic chloride
CALCIUM	Ca	40·21	251·31	Marignac	CaO, lime; $CaCl_2$, calcic chloride
CARBON	C	12	75	Dumas and Stas	CO_2, carbonic anhydride; CH_4, marsh gas
Cerium	Ce	94·52	590·75	Marignac (Bunsen, 92)	Ce_2O_3, ceric oxide; $CeCl_2$, cerous chloride
CHLORINE	Cl	35·46	221·62	Stas (Dumas, 35·505)	HCl, hydrochloric acid
Chromium	Cr	52·5	328·12	Peligot	Cr_2O_3, green oxide; Cr_2Cl_6, violet chloride
Cobalt	Co	58·8	367·5	Russell (Winkler, 58·99)	CoO, cobaltous oxide; $CoCl_2$, cobaltous chloride
COPPER (Cuprum)	Cu	63·29	395·56	Berzelius	CuO, black oxide; $CuCl_2$, cupric chloride
Didymium	D	96	600	Marignac	DO, oxide
Erbium	E	112·6	703·75	Bunsen and Bahr (Clève and Hoeglund, 113·7)	EO, erbia
Fluorine	F	19	118·75	Louyet	HF, hydrofluoric acid
Gallium	Ga			Lecoq de Boisbaudran	Ga_2Cl_6, chloride; ammonium gallium alum
Glucinum	G	9·29	58·06	Awdejew	GO, glucina; GCl_2, glucinic chloride
Gold (Aurum)	Au	196·66	1229·12	Berzelius	$AuCl_3$, auric chloride
HYDROGEN	H	1	6·25		H_2O, water; HCl, hydrochloric acid
Indium	In	113·41	708·81	Winkler	In_2O_3, indic oxide; indium-ammonium alum $(NH_4)_2SO_4,In_2(SO_4)_3,24H_2O$
IODINE	I	126·85	792·81	Stas	HI, hydriodic acid
Iridium	Ir	198·44	1240·25	Berzelius	Ir_2O_3, iridic oxide; $IrCl_3$, tri-chloride
IRON (Ferrum)	Fe	56·08	350·5	Berzelius (Dumas, 56·14)	Fe_2O_3, red oxide; Fe_2Cl_6, ferric chloride
Lanthanum	La	94·13	588·31	Marignac (Zschiesche, 90·18)	LaO, oxide; $LaCl_2$, chloride
LEAD (Plumbum)	Pb	206·91	1293·19	Stas (Dumas, 207·1)	PbO, litharge; $PbCl_2$, plumbic chloride
Lithium	L	7·02	43·87	Stas	L_2O, lithia; LCl, lithic chloride
MAGNESIUM	Mg	24·60	153·75	Dumas (Marchand & Scheerer, 24·04)	MgO, magnesia; $MgCl_2$, magnesic chloride
MANGANESE	Mn	55·1	344·37	Berzelius (Dumas, 54·96)	MnO_2, black oxide; $MnCl_2$, manganous chloride
MERCURY (Hydrargyrum)	Hg	200·2	1251·25	Erdmann and Marchand	HgO, red oxide; $HgCl_2$, corrosive sublimate

Molybdenum	Mo	96	600	Dumas	MoO_3, molybdic anhydride
Nickel	Ni	58·7	366·87	Russell (Winkler, 59·06)	NiO, nickelous oxide; $NiCl_2$, chloride
Niobium (Columbium)	Nb	94·0	587·5	Marignac	Nb_2O_5, niobic anhydride; $NbCl_5$, chloride
NITROGEN	N	14·04	87·75	Stas (Anderson and Svanberg, 13·95)	H_3N, ammonia; HNO_3, nitric acid
Osmium	Os	198·8	1242·5	Berzelius	OsO_4, volatile oxide
OXYGEN	O	16	100		H_2O, water
Palladium	Pd	106·48	665·5	Berzelius	$Pd(NO_3)_2$, palladious nitrate; PdO, palladious oxide
PHOSPHORUS	P	31	193·75	Schrötter (Dumas, 31·03)	H_3P, phosphuretted hydrogen; P_2O_5, phosphoric anhydride
Platinum	Pt	197·12	1232	Berzelius	$PtCl_4$, platinic chloride
POTASSIUM (Kalium)	K	39·137	244·6	Stas	KHO, caustic potash
Rhodium	Ro	104·32	652	Berzelius	NaCl, $RoCl_3$, double chloride
Rubidium	Rb	85·36	533·5	Bunsen (Piccard, 85·41)	RbHO, caustic rubidia; RbCl, rubidic chloride
Ruthenium	Ru	104·22	651·37	Claus	RuO_3, ruthenic anhydride
Selenium	Se	79·46	496·62	Dumas	SeO_2, selenious anhydride
SILICON	Si	28·5	178·12	Pelouze (Dumas, 28·02)	SiO_2, silica; $SiCl_4$, silicic chloride
SILVER (Argentum)	Ag	107·93	674·56	Stas	Ag_2O, oxide; AgCl, argentic chloride
SODIUM (Natrium)	Na	23·043	144·19	Do.	NaCl, common salt; NaHO, caustic soda
Strontium	Sr	87·54	547·12	Marignac (Dumas, 87·53)	SrO, strontia; $SrCl_2$, strontic chloride
SULPHUR	S	32·074	200·46	Stas	H_2SO_4, oil of vitriol; H_2S, sulphuretted hydrogen
Tantalum	Ta	182	1137·5	Marignac	Ta_2O_5, tantalic anhydride; TaF_5, tantalic fluoride
Tellurium	Te	128·3	801·87	Berzelius (Dumas, 129)	H_2Te, telluretted hydrogen
Thallium	Tl	204	1275·0	Lamy (Crookes, 203·6)	Tl_2O, oxide; TlCl, thallious chloride; $TlCl_3$, thallic chloride
Thorinum	Th	115·7	723·12	Delafontaine	ThO, thorina; $ThCl_2$, thorinic chloride
Tin (Stannum)	Sn	118·06	737·87	Dumas	SnO_2, tin stone; $SnCl_4$, stannic chloride
Titanium	Ti	50·34	314·62	Pierre	TiO_2, rutile; $TiCl_4$, liquid chloride
Tungsten (Wolfram)	W	184·1	1150·06	Dumas	WO_3, tungstic anhydride
Uranium	U	120	750	Peligot	U_2O_3, uranic oxide
Vanadium	V	137·1	856·8	Berzelius (Roscoe, 51·2)	VO_3, vanadic anhydride; VCl_3, vanadic chloride (vanadic anhydride, V_2O_5; oxychloride, $VOCl_3$, Roscoe)
Yttrium	Y	59·7	373·12	Clève and Hoeglund	YO, yttria; YCl_2, yttric chloride
ZINC	Zn	65·04	406·5	A. Erdmann	ZnO, zincic oxide; $ZnCl_2$, zincic chloride
Zirconium	Zr	89·5	559·37	Berzelius	ZrO_2, zirconia, ZrF_4, zirconic fluoride

Berzelius, to whom we are indebted for the fundamental determinations of the atomic weights of the elements, referred them all to 100 parts of oxygen. In the foregoing table, for convenience of comparison, a column is added containing the corresponding numbers on the oxygen scale, when this standard is followed, which, however, is now generally abandoned. The names of the most important of the elements, 22 in number, are printed in capitals; those of small importance or rare occurrence, 27 in number, in italics. The numbers representing the atomic weights are those actually obtained by experiments conducted with all the refinements which the most scrupulous exactness could suggest. The researches of Stas in particular furnish a model for investigations of this nature. For practical purposes many of these numbers may be represented by others which are usually multiples by an integer of the atomic weight of hydrogen. Prout advanced the hypothesis that all the elementary substances had atomic weights which were multiples by a whole number of that of hydrogen, and the researches made in this direction within the last twenty years have had chiefly in view the verification or disproof of this hypothesis. This subject is considered more fully in the concluding chapter of the second volume. The numbers used in this volume are given in the table facing page 1.

of chemical changes, since it greatly abridges the labour of description, and after a little practice, enables the student to trace at a glance, reactions even of a complicated character. Its use has, in fact, become indispensable both to the teacher and to the pupil.

Every elementary substance is represented by a symbol, consisting of the first letter of its Latin name; in cases where more than one element has the same initial, a second distinguishing letter is added. Any symbol, when it stands alone, always represents one atom of the body which it indicates. For instance, the symbol O stands for one *atom* of oxygen; H, for one *atom* of hydrogen; C, for one *atom* of carbon, and so on. The symbols appropriated to the various elements are placed opposite to them in the column headed *Symbols* in the preceding table.

It must be borne in mind that the notation employed by chemists is not a true algebraic notation, although it resembles it in appearance. For example, the juxtaposition of two chemical symbols constitutes a *chemical formula*; such juxtaposition, however, indicates chemical combination, not multiplication; so that a compound body is represented by writing the symbols of its constituent atoms side by side; for example, HCl indicates one *molecule* of hydrochloric acid, CaO one *molecule* of lime, the quantities included in each formula always indicating one molecule of the compound.

If it be necessary to express that more than one atom of a body enters into the formation of a molecule, the object is attained by writing a small figure to the right of the symbol below the line;—H_2 would indicate a molecule of hydrogen; H_2O_2, a molecule of hydric peroxide, composed of 2 atoms of hydrogen and 2 of oxygen; CO_2, one molecule of carbonic anhydride, composed of 1 atom of carbon and 2 atoms of oxygen, and so on. Some authors place the small figures above instead of below the line, and write 2 atoms of hydrogen, for example, as H^2.

Secondary compounds, such as salts, are expressed in an analogous way, the metal being usually placed first, $CaCO_3$ representing one molecule of calcic carbonate. When a comma is used to separate two members of a formula, these two members are represented as united chemically, and a more intimate union is supposed than when the sign of a period is used to separate them. For instance, in the formula for crystallized sulphate of magnesium and potassium ($MgSO_4,K_2SO_4 . 6H_2O$), the compound $MgSO_4$ is supposed to be more intimately united with K_2SO_4 than the $6H_2O$, which may be readily expelled by heat. Where it is necessary

to indicate more than one molecule of a compound, the whole formula of that compound is preceded by the indicating number. If, for example, H be 1 atom of hydrogen, H_2 its molecule, $3H_2$ will indicate 3 molecules of hydrogen. If brackets be used, the figure prefixed or subjoined, multiplies nothing beyond the symbols included within the brackets, as for example, 3 ($MgSO_4$, $7\,H_2O$), three molecules of crystallized magnesic sulphate; $(H_3N)_4$, four molecules of ammonia. The use of brackets is often neglected, and then the figure prefixed multiplies all the symbols included between it and the next comma or period, or sign of addition or of equality.

The sign + should never be used to connect together the constituents of the same compound, but should be employed only to indicate cases of true addition, in which two different bodies are actually mixed with each other, although many chemists neglect, with manifest inconvenience, to attend to this rule. The sign = does not indicate identity or absolute equality, but is usually employed in the sense of the word 'yields;' and when placed between the two members of an equation, it indicates that if the compounds which precede it are mixed with due precaution, the result of the chemical changes which occur will be such as is represented by the arrangement of the symbols placed after the sign =.

A little practice will make these various modifications familiar to the mind. To expedite the acquisition of this knowledge, the student will find it advantageous to exercise himself in the expression of chemical changes by symbols, whenever the opportunity occurs, until he is thoroughly acquainted with their signification and use.

(14) *Law of Volumes.*—When bodies are capable of assuming the form of gas or vapour, a very simple relation exists between the volumes of any two gases which combine together, and the volume of the gaseous compound formed by their union. This important observation is due to Gay-Lussac. It has been found, for example, that two gases unite together either in the proportion of equal volumes, or else that two volumes of a given gas which may be distinguished as A, combine with one volume of a second gas which may be called B, or that three volumes of A unite with one of B, or sometimes that three volumes of A unite with two of B. Some simple ratio of this kind is always observed between the volumes of two gases which enter into combination. The cause of this uniformity depends upon the fact that if quantities of each element be compared in the ratio of their *atomic*

weights, when converted into vapour (under similar conditions of temperature and pressure) they will all yield the same volume of vapour, except in the cases of mercury, cadmium, and zinc, which give double the volume, and phosphorus and arsenic, which yield one half of the volume of the corresponding quantity of hydrogen.

For example, in the following table we take a number of grammes of hydrogen, of nitrogen, of oxygen, and of chlorine, corresponding with the atomic weight of each element respectively, and the result is in all cases a volume of 11·16 litres:—

	Litres.
1 gramme of hydrogen, at {32° F. and 29·922 inches Bar. (or 0° C. & 760 millim.)}	= 11·16
14 grammes of nitrogen	= 11·16
16 grammes of oxygen	= 11·16
35·5 grammes of chlorine	= 11·16

and so on.

In other words, gaseous nitrogen is 14 times as dense as hydrogen, oxygen 16 times as dense, and chlorine 35·5 times as dense as hydrogen, when compared under equal pressures, and at the same temperatures.

In order to facilitate the calculation of the weight of a volume of gas, Dr. Hofmann has proposed the use of a unit which he calls the *crith* (from κριθή, a barley-corn). This is the weight of a litre of hydrogen at 0° C. and 760 millim. Bar. or 0·0896 gramme. One litre of nitrogen will therefore be 14 criths or 0·0896 × 14 = 1·2544 gramme.

Combination by volume, therefore, is to be carefully distinguished from combination by weight; because when the volumes are the same the weights are different, and when the weights are the same the volumes are different.

After the union of the gases with each other, the volume of the compound, though it is often less than the joint volume of the two separate gases, yet bears a simple relation to it. It may happen that two gases unite without undergoing any change of volume; this only occurs when the constituent gases combine in equal volumes; in other cases three volumes of the gases may become condensed into two; or three volumes may occupy one volume; or, again, two volumes may be condensed into one volume. In no case do the combined gases occupy a larger volume than they did when separate.

The mode of combination of hydrogen with chlorine and with oxygen may be taken as an illustration of some of these points.

Hydrogen gas and gaseous chlorine unite in the ratio of one volume of each to form hydrochloric acid, or one part *by weight* of hydrogen to 35·5 parts by weight of chlorine, the two gases after their combination still occupying two volumes, or the same volume which they did when separate, though their united weight is of course 36·5. But when hydrogen gas combines with oxygen gas in the formation of water, union takes place in the ratio of two volumes of hydrogen to one volume of oxygen. This, therefore, corresponds by weight to 2 parts of hydrogen and 16 of oxygen. Supposing that the two gases before their union were heated to a temperature above the boiling-point of water, say to 120° C., and the product of the combination after union is still kept at the same temperature, the steam produced, instead of occupying three volumes, becomes condensed into two; but the weight of the steam formed is equal to that of the united weights of the oxygen and hydrogen which have entered into its composition.

Compound gases and vapours, in combining, follow the same regularity and simplicity in the ratios by volume in which they unite, as is observed to prevail among elementary bodies; and the compounds resulting from such union, when gaseous, or convertible into vapour, exhibit the same equally simple ratio in volume to that of their components.

In order to give precision to our language, although it would be premature at this point to enter into the reasons in detail, it will be convenient here to draw a distinction between two magnitudes of the component particles of all elementary bodies—viz.: 1. the *Atom*, or smallest and chemically-indivisible particle of each element which can exist in a *compound*, united with other particles either of the same or of different elements, but which is not known in a separate form except in the cases of some elements such as mercury and cadmium; and 2, the *Molecule* or the smallest quantity of any elementary substance which is capable of existing in a *separate form*. H, for instance, represents the *atom* of hydrogen, whilst HH, or H_2, indicates its *molecule*. Each molecule of chlorine and of the other allied elements, when in the gaseous state, appears to consist of 2 atoms. Assuming that the molecule of any element in vapour always occupies 2 volumes, the atom of hydrogen being 1 volume □, or (H = 1), the molecules of oxygen, sulphur, selenium, and tellurium, each contain 2 atoms; but certain metals, such as mercury and cadmium, yield a vapour the molecule of which contains only a single atom of the element; and if it were possible to make the experiment with the other analogous metals—magnesium, copper, &c.—it is

probable that the molecule of each member of this class of elements would be found to contain but a single atom.

The molecule of nitrogen contains 2 atoms; but the molecules of phosphorus and of arsenicum each contain 4 atoms. Analogy leads to the conclusion that the molecules of antimony and of bismuth also each contain 4 atoms.

Some of these relations are indicated in the following table:—

Element.	Atomic Weight.	Molecular Weight.	Mol. Vol.	Relative Weight.
Hydrogen . . .	H = 1	H_2 = 2		1
Chlorine . . .	Cl = 35·5	Cl_2 = 71		35·5
Oxygen	O = 16	O_2 = 32		16
Sulphur	S = 32	S_2 = 64		32
Selenium . . .	Se = 79·5	Se_2 = 159		79·5
Tellurium . . .	Te = 129	Te_2 = 258		129
Mercury . . .	Hg = 200	Hg = 200		100
Cadmium . . .	Cd = 112	Cd = 112		56
Zinc	Zn = 65	Zn = 65		32·5
Nitrogen . . .	N = 14	N_2 = 28		14
Phosphorus . .	P = 31	P_4 = 124		62
Arsenic	As = 75	As_4 = 300		150

The application of the terms atom and molecule may be extended to compound substances, the *atom of a compound* being the smallest quantity of any compound substance which is capable of existing in combination with other particles of matter; and the *molecule of a compound* is, as before, the smallest quantity of that substance which can exist in an isolated or separate condition: if, for instance, C_2H_5 represent the compound atom of ethyl (the radicle of ether), (C_2H_5, C_2H_5), or $(C_2H_5)_2$, would indicate its molecule.

Since the terms *atom* and *compound* are usually employed to indicate precisely opposite things (a compound being divisible and an atom indivisible), it will be necessary to guard against a misunderstanding of the expression *atom of a compound*. For this purpose some chemists call the quantity of ethyl represented by C_2H_5 the *semi-molecule;* in the same way that H represents the semi-molecule of hydrogen. The semi-molecule, which in this case corresponds to the atom of an element such as hydrogen or chlorine, is not always the quantity of a compound which exists in combination: for just as the atom and molecule of

cadmium and mercury are of the same weight, so some compounds, such as ammonia, NH_3, and ethylene, C_2H_4, unite by molecules and not by semi-molecules.

It will be shown hereafter that equal volumes of every gas and vapour, whether simple or compound, expand equally for equal increments of heat, if both are compared at the same temperatures (134). The same is true when equal volumes of the different gases are submitted to an equal increase or diminution of pressure (27). Hence it appears to be a legitimate and necessary conclusion that equal volumes of all gases, whether simple or compound, contain an equal number of molecules of their constituents.

The volume of the *molecule* of a compound body, in the aëriform state, is exactly double the volume of the *atom* of hydrogen. To this rule, indeed, there are some exceptions, real or apparent; but the number of these is gradually diminishing, under the explanations afforded from time to time by the progress of science.

When the complicated bodies met with in organic chemistry admit of being vaporized without undergoing decomposition, they obey this law of vapour volume as strictly as the simplest combinations of inorganic nature, however numerous the atoms which enter into the formation of their molecule. A molecule of alcohol (C_2H_6O), or a molecule of the still more complex body aniline (C_6H_7N), for instance, yields the same volume of vapour as a molecule of hydrochloric acid (HCl). Consequently, if the weight of a given bulk of hydrogen, the lightest substance known, be taken as the unit of comparison, the vapour density of a compound body is represented by half its molecular weight. This number will be designated constantly hereafter, in speaking of vapour densities as the *relative weight* of the vapour. For example:—

	Equal vols.		Molecular weight.	Relative weight.
Hydrogen gas . . .	(HH)		2	1
Hydrochloric acid gas	(HCl)		36.5	18·25
Aqueous vapour . .	(H_2O)		18	9
Alcohol vapour . .	(C_2H_6O)		46	23
Aniline vapour . .	(C_6H_7N)		93	46·5

(15) *Applications of the Law of Combining Proportion or Combining Ratio.*—Compound bodies unite with other compounds, just as simple bodies unite with other simple ones, and the combining proportions or molecular weights of such compounds are

represented by the sum of the atomic weights of all the elements which enter into their composition; the molecular weights of the compound can never be less than that sum, but sometimes it is a multiple of that number. For example, the molecular weights of the following compounds are thus obtained:—

Hydrochloric acid	(1 At. H = 1 + 1 At. Cl = 35·5)	HCl = 36·5
Ammonia	(3 At. H = 3 + 1 At. N = 14)	H_3N = 17·0
Common salt (sodic chloride)	(1 At. Na = 23 + 1 At. Cl = 35·5)	$NaCl$ = 58·5
Water	(2 At. H = 2 + 1 At. O = 16)	H_2O = 18·0
Anhydrous potash	(2 At. K = 78·2 + 1 At. O = 16)	K_2O = 94·2
Potassic hydrate	(1 At. K = 39·1 + 1 At. H = 1 + 1 At. O = 16)	KHO = 56·1
Ammonia hydrochlorate	(1 Mol. H_3N = 17 + 1 Mol. HCl = 36·5)	H_3N, HCl = 53·5

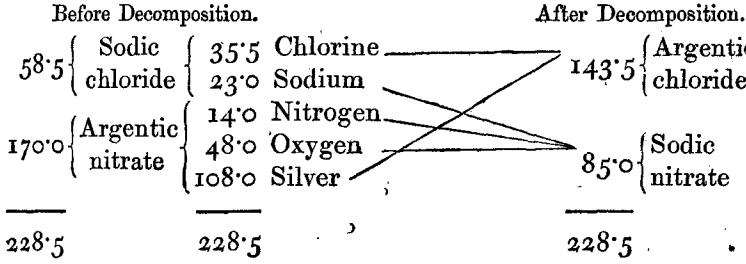
The law of combining proportions holds good not only between the compounds formed by the union of simple substances with each other, but also between the bodies formed by the combination of compound substances with other compounds. Indeed, the reactions between compounds often exhibit very striking exemplifications both of the generality of this law and of the manner in which it may be turned to useful account. The following example of the reaction between common salt, or sodic chloride, and argentic nitrate, will afford an illustration of this kind.

Sodic chloride is a compound of 1 atom or 23 parts of sodium and 1 atom or 35·5 parts of chlorine: its molecular weight is therefore 58·5. In like manner, argentic nitrate consists of 1 atom or 108 parts of silver, 1 atom or 14 parts of nitrogen, and 3 atoms or 48 parts of oxygen, forming together 170, which we should expect to represent its molecular weight. This salt, when dissolved in water, is without action upon either red or blue litmus paper. Common salt is likewise perfectly neutral in its reactions upon coloured tests.

If we mix together a solution of 58·5 milligrammes of sodic chloride with a solution of 170 mgrms. of argentic nitrate, a very instructive result is obtained: the sodium and the silver change places; the nitrogen and oxygen unite with the sodium to form sodic nitrate; and the chlorine unites with the silver to form argentic chloride. This chloride is insoluble, and is therefore precipitated in white flocculi. But the remarkable point is, that there is neither more nor less of the nitrogen and oxygen than is required by the sodium, neither more nor less chlorine than will combine with the silver: 35·5 mgrms. of chlorine are chemically equivalent to the 62 mgrms. of nitrion (NO_3), and

may be substituted for them in combination; and 108 mgrms. of silver are as truly equivalent to 23 of sodium.

This interchange, or *double decomposition* as it is often termed, is illustrated by the diagram that follows:*



The solutions after mixture are still without action upon either blue or red litmus paper.

If instead of using exactly the equivalent quantities of the two salts, an excess of either had been employed,—say that 200 instead of 170 milligrammes of argentic nitrate had been used,—this excess of 30 mgrms. would not have influenced the result, but would have remained unchanged in the solution. One great advantage, therefore, that is derived from the employment of a table of atomic weights, is economy in the use of the materials employed in the formation of compounds, since by its means it is possible to calculate the exact proportions of the chemical agents required to obtain the full effect of their mutual reaction.

The law of combining proportions also forms the basis upon which most of the calculations in chemical analysis are founded. Suppose it were desired to ascertain the proportion of silver present in the solution of argentic nitrate. By collecting on a filter the precipitate produced on adding sodic chloride in slight excess to a given volume of the liquid, then washing, drying, and weighing the powder with suitable precautions, the quantity of silver can be at once calculated; for it is a necessary consequence of the law of combination that every 143·5 mgrms. of chloride of silver contain 108 mgrms. of silver. From this result the proportion of argentic nitrate in the solution could also be deduced

* The same changes may be represented in a single line by the use of symbols, which, if the atomic weights of the various elements be remembered, convey the same information as a detailed description: *e.g.*:—

$$\overbrace{NaCl}^{\text{Sodic chloride.}} + \overbrace{AgNO_3}^{\text{Argentic nitrate.}} = \overbrace{AgCl}^{\text{Argentic chloride.}} + \overbrace{NaNO_3}^{\text{Sodic nitrate.}}$$

with equal ease, inasmuch as 108 mgrms. of silver require for conversion into nitrate 62 mgrms. of nitrion, and therefore represent 170 mgrms. of argentic nitrate; consequently 143·5 mgrms. of argentic chloride indicate the presence of 170 mgrms. of argentic nitrate in the liquid under examination.

(16) *Equivalency of the Elements.*—From what has been already stated (p. 23) it is clear that the atom of one element is by no means necessarily equivalent in chemical power to the atom of another element. The most recent investigations, in fact, show that the elementary bodies may be arranged in groups, according to their chemical equivalency in relation to hydrogen, as follows—viz. :—

1. *Monads,* or *Uniequivalent* Elements, in which one atom of each in combination is usually equivalent to H, or one atom of hydrogen. In these the atomic and equivalent numbers are identical.

2. *Dyads,* or *Biequivalent* Elements, in each of which one atom, in combining with other bodies, is generally equivalent to H_2, or two atoms of hydrogen. In these the atomic number is double the equivalent number.

3. *Triads,* or *Terequivalent* Elements, in each of which one atom, in entering into combination with other bodies, is generally equivalent to H_3, or three atoms of hydrogen.

4. *Tetrads,* or *Quadrequivalent* Elements, each of which in combining represents H_4, or four atoms of hydrogen.

5. *Pentads,* or Elements, each of which in combining represents 5 atoms of hydrogen.

6. *Hexads,* or Elements, each atom of which in combining may represent 6 atoms of hydrogen.

Occasionally it will be found convenient to indicate the equivalent power of an element by affixing dashes or Roman numerals to the symbols. Ca″, for example, would indicate the biequivalent power of the proportion of calcium represented by its symbol; P‴ would indicate the terequivalent power of phosphorus; Sn^{iv} the quadrequivalent power of tin, and so on.

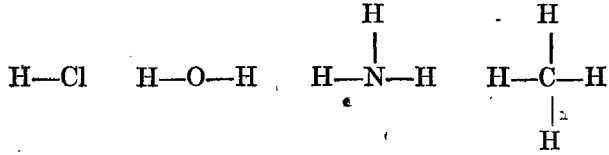
In the following table the principal elements are arranged into six groups upon the principle just indicated :—

MONADS. Elements equivalent to 1 atom of hydrogen.	DYADS. Elements equivalent to 2 atoms of hydrogen.	TRIADS. Elements equivalent to 3 atoms of hydrogen.	TETRADS. Elements equivalent to 4 atoms of hydrogen.	PENTADS. Elements equivalent to 5 atoms of hydrogen.	HEXADS. Elements equivalent to 6 atoms of hydrogen.
Hydrogen	Oxygen	Gold	Carbon	Nitrogen	Molybdenum
Fluorine	Sulphur	Rhodium	Silicon	Phosphorus	Tungsten
Chlorine	Selenium	Boron	Titanium	Vanadium	Osmium
Bromine	Tellurium	Thallium	Tin	Arsenic	Chromium
Iodine	Barium		Zirconium	Antimony	Manganese
Lithium	Strontium		Thorinum	Bismuth	Iron
Sodium	Calcium		Lead	Niobium	
Potassium	Magnesium		Platinum	Tantalum	
Rubidium	Zinc		Palladium		
Cæsium	Cadmium		Iridium		
Silver	Copper		Ruthenium		
	Mercury		Aluminium		
	Lanthanum		Indium		
	Didymium		Gallium		
	Glucinum		Cobalt		
	Yttrium		Nickel		
	Erbium		Cerium		
			Uranium		

(16 *a*) *Atomicity of the Elements.*—The elements of these six groups have also different combining or atom-fixing powers. Thus one atom of a monad, can only be united to one atom of another monad in a compound, as in the case of hydrochloric acid, where an atom of chlorine is united with one of hydrogen. The dyads are capable of fixing two monad elements, as in water, consisting of one atom of oxygen combined with two of hydrogen. Again, triad nitrogen in ammonia is united with three atoms of hydrogen; and in ammonic chloride the same element has pentad functions, being combined with four atoms of hydrogen and one of chlorine. Thus, if we have one molecule of a compound containing one atom of an element (of which the atom-fixing power or atomicity is unknown) united with hydrogen or other monads, we can usually measure the atomicity of the element by the number of monads present; for, since we have no evidence that these monads can unite with more than one other element at one time, we can only explain the existence of such compounds as ammonia, NH_3, or marsh gas, CH_4, by supposing that the three atoms of hydrogen in the former and the four of hydrogen in the latter are directly united with the nitrogen and carbon respectively. The atom of nitrogen thus appears to have three combining powers or points of attachment, or bonds which enable it to unite with three monad elements at the same time; similarly, carbon has four such bonds; oxygen two, while hydrogen and the other monads have only one. The greatest precaution must be taken against

allowing the mind to imagine that there is any *material* connecting link between atoms in chemical compounds; all that the term bond is intended to imply is a connexion similar to that existing between the members of the solar system; and without the supposition of the existence of some such force it is difficult to account for the stability of chemical substances.

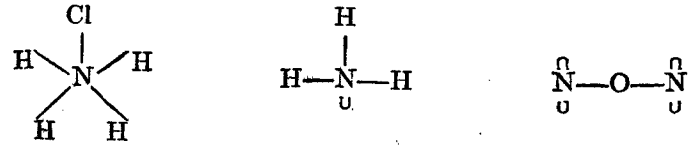
To assist in comprehending the constitution of compounds, chemists have adopted a form of graphic representation of the bonds of the elements. The symbols of the elements in a compound are joined to one another by lines, the symbol of a monad element having one line, a dyad two, and so on. Thus, H—O— —N< —C< The compounds hydrochloric acid, water, ammonia and marsh gas, would be represented by



The position of the lines is of course immaterial, the only important things to be observed are their number, and the elements to which they are attached. Thus carbonic anhydride may be written O=C=O or O⌒C⌒O.

The atomicity of an element appears to be variable to a certain extent; thus nitrogen is pentad in ammonic chloride, triad in ammonia and monad in nitrous oxide, but it will be noticed that this variation takes place by the suppression of two bonds at a time, and it is quite easy to imagine that these attractions neutralize or saturate one another; so that the three compounds named might be thus formulated:—

Ammonic Chloride. Ammonia. Nitrous Oxide.



The maximum or absolute atomicity of nitrogen is said to be 5, all the attractive forces being active in ammonic chloride; in ammonia three are active and two latent; and in nitrous oxide one is active in each atom of nitrogen and four latent.

To bring the symbolic mode of representing chemical compounds into relation with the graphic notation, Dr. Frankland has proposed that the symbol of the element having the highest atomicity should be placed at the commencement of the formula, and to show that the other elements of the compound are directly combined with this binding element its symbol is printed in a thicker type. Thus the symbolic formulæ for the seven compounds above mentioned would be:—

HCl or ClH	OH_2	NH_3	CH_4	CO_2	NH_4Cl	ON_2
Hydrochloric acid.	Water.	Ammonia.	Marsh gas.	Carbonic anhydride.	Ammonic chloride.	Nitrous oxide.

The details of this introductory chapter are necessary to the student at the commencement of his chemical course; but the full consideration of some of the subjects here alluded to, such as the determination of the atomic weights, and the discussion of the equivalency of the elements, will be resumed as preliminaries to the study of organic chemistry.

CHAPTER II.

WEIGHTS AND MEASURES—DENSITY.

(17) *Weights and Measures.*—The foundation of all accuracy in experimental science consists in the possibility of determining with exactness the quantity or mass, and the size or volume of those substances which are submitted to examination. In gravity we possess an unvarying standard of comparison.

Gravity diminishes slowly from the pole to the equator. A mass of matter which would compress a spring with a force equal to that of 194 at the equator, would act upon it with a force of about 195 at the poles. This difference would not, of course, be perceived in the ordinary mode of weighing by the balance, as both the weights and the body weighed would be similarly and equally affected.

The common process of weighing consists in estimating the attraction with which any given mass is drawn towards the earth, by comparison with other known quantities of matter, arbitrarily selected for the purpose; consequently, the *weight* of a body is the expression in terms of the standard so selected, of the exact amount

of tension or pressure which is required to prevent the body under examination from falling to the ground.

The standard of mass or weight used in this country is an arbitrary quantity called the avoirdupois pound, which is subdivided into 7000 grains. It was enacted in 1855, 'that the platinum weight deposited in the Exchequer shall be denominated the Imperial standard pound avoirdupois, and that the $\frac{1}{7000}$th of it shall be a grain, while 5760 such grains shall denote one pound troy.'

The system of weights is connected with the measures of volume in use in this country, through the medium of the Imperial gallon; which is defined by an Act of Parliament of the year 1824 to be a measure containing 10 lb. avoirdupois of distilled water weighed in air at a temperature of 62° F., the barometer standing at 30 inches. The gallon of distilled water, therefore, contains 70,000 grains.

These measures of volume are related to those of length by the determination that a gallon contains 277·276 cubic inches. A cubic inch of distilled water weighs, in air at 62°, with the barometer at 30 inches, 252·456 grains; *in vacuo* (24) it weighs 252·722 grains. The standard of length is the yard measure, and is subdivided into 36 inches.* The standard yard is defined by an Act of Parliament passed in 1855, whereby it is enacted, 'that the straight line or distance between the centres of two gold plugs in the bronze bar deposited in the office of the Exchequer shall be the genuine standard yard at 62° Fahr., and if lost it shall be replaced by means of its copies.'

(18) *French or Metrical System of Weights and Measures.*—The French system of weights and measures is connected together in a manner far more philosophical than the foregoing; it is the one generally adopted by scientific men abroad, and is now being introduced into the writings of men of science in this country. Its advantages indeed are so great that it will be largely used in this work.†

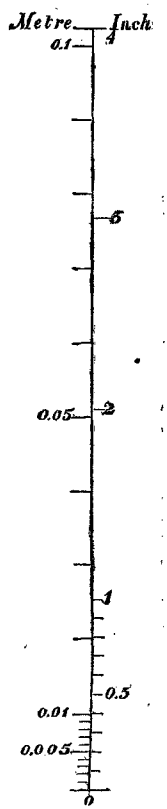
* In order further to connect the measures of length with those of weight, Captain Kater determined the length of a seconds pendulum, the oscillations of which are produced by the action of gravity. The length of a pendulum, which beats seconds at the level of the sea *in vacuo*, and in the latitude of Greenwich, he found to be 39·13929 inches. See also the reports of Prof. W. H. Miller on the standard pound (*Phil. Trans.* 1856, 753), and of Mr. (now Sir George) Airy on the new standard of length (*Phil. Trans.* 1857, 621).

† The repugnance experienced by most persons to adopt a new system of weights and measures arises chiefly from the difficulty of mentally realizing the values of the new denominations in terms of those to which the mind is accus-

The principles on which the metrical system is based are the following :—

The standard of reference is a measurement of one of the great circles encompassing the earth itself. The ten-millionth part of a quadrant of the meridian constitutes the unit of the system. This quadrantal arc was fixed at 6213 miles and 1450 yards English measure; consequently the ten-millionth part of this, the *metre*, is equivalent to 39·37079 English inches, nearly $3\frac{1}{2}$ inches more than our standard yard, or a fraction of an inch longer than the seconds pendulum.* Multiples of the metre are designated by the Greek prefixes *deca, hecto, kilo,* signifying 10, 100, and 1000 respectively, the decametre, for instance, being 10 metres. On the other hand, the subdivisions of the metre are indicated by the corresponding Latin prefixes, *deci, centi,* and *milli,* so that the tenth of a metre is called a *decimetre*; the hundredth, a *centimetre;* and the thousandth, a *millimetre.* A millimetre amounts very nearly to $\frac{1}{25}$ of an English inch, and a centimetre to nearly $\frac{2}{5}$ of an inch, 2 inches being a little over 5 centimetres. A *kilometre,* or thousand metres, nearly $\frac{2}{3}$ of an English mile, is employed in many parts of France as the ordinary road measure. Fig. 3 represents a decimetre subdivided into centimetres, one of which is subdivided into millimetres, compared with English inches.

FIG. 3.



Measures of surface, as for land measure, are connected with the measures of length by taking as the unit of the surface the

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tomed. Nothing but the actual employment of the weights and measures themselves in practice can effect this thoroughly; but it is useful to carry about with one a small rule divided on one side into inches, on the other into millimetres. No one who has once fully experienced the advantage of systematically applying the decimal correlated weights and measures in calculations, will voluntarily resume the cumbrous and artificial method which we use in this country. A line of type in this work is 4 inches long, or just over 10 centimetres in length. It may, therefore, furnish a ready standard of comparison to the mind until the student is completely familiar with the metrical equivalents to the inches to which he is accustomed. In the Appendix to this volume will be found some tables designed to facilitate the calculation of the metrical values into their equivalent English representatives, and *vice versâ.*

* More accurate geodetic measurements have since shown that there is an error of more than a mile and a half in this determination, but the value of the

area of a square decametre, each side of the square measuring 10 metres; such an area constitutes the *are*, whilst 100 such units constitute the *hectare*, or ordinary land measure, corresponding to nearly 2½ English statute acres.

In measuring the cubic contents of a stack of wood, or other rough articles, the unit employed is the cubic metre, or *stere*, from στερεὸς, solid.

For the purposes of exact measurement, however, the measures of volume are connected with those of length by making the unit of capacity in this series a cube of a decimetre, or 3·937 English inches, in the side; this, which is termed a *litre*, is equal to 1·7637 Imperial pints, or rather more than 1¾ English pints. The litre is again subdivided into tenths, or *decilitres*, and hundredths, or *centilitres*.

Finally, the system of weights (or mass) is connected with both the preceding systems, by taking as the unit a cubic centimetre of distilled water, at the temperature of 4° C. (39°·2 F.); it contains 15·432 English grains. The *gramme*, as this quantity is called, is further subdivided into tenths, or *decigrammes*; hundredths, or *centigrammes*; and thousandths, or *milligrammes*; and its higher multiple, 1000 grammes, forms the *kilogramme*. The kilogramme is the commercial unit of weight or mass, and is something less than 2¼ lb. avoirdupois, being 15432·3 English grains. (W. H. Miller, *Phil. Trans.* 1856, 893.) The milligramme is equal to nearly $\frac{1}{65}$ of a grain, or 1 grain to 65 milligrammes. The litre, as it consists of 1000 cubic centimetres of water, at 4° C., contains exactly a kilogramme of water, and is equivalent, at 4° C., to 61·024 cubic inches English.

(18 *a*) *Unit of Force.*—In many physical inquiries a unit of force is employed to indicate results obtained, and which shall be the same everywhere. The unit recommended by the Committee of the British Association appointed for the Selection and Nomenclature of Dynamical and Electrical Units, is called the *dyne*. It is that force which, acting on a gramme for a second, produces a velocity of a centimetre per second. Thus, a mass falling towards the earth at the latitude of Greenwich, acquires a

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metre remains unaffected by this fact, though it is not really the exact ten-millionth of the quadrantal arc. This, however, does not in the slightest degree affect the system of weights and measures founded on the metre. It merely furnishes an additional reason in support of the opinion that every system of measure, to be permanent, must be founded not upon an abstract quantity, but upon a comparison with some material bar which is arbitrarily defined to be the unit of the system.

velocity of 981·17 centimetres per second at the end of the first second of its fall; if the mass falling be a gramme, the force acting upon it is said to be 981·17 dynes. (See Everett's *Illustrations of the Centimetre-gramme-second System of Units*, published by the Physical Society, 1875.) The unit of force which is obtained from the gravitation of a certain mass is called a *gravitation unit*, and varies for different places.

(19) *The Balance.*—The familiar operation of weighing is for the most part effected by means of the balance.

This instrument consists essentially of an inflexible bar, delicately suspended at a point exactly midway between its extremities, from which depend the scale-pans; in one of these the weights, in the other the objects to be weighed, are placed. When the balance is *in equilibrio*, the arms of the beam assume a direction perfectly horizontal. The main points requiring attention are—1st, Equality in the length of the arms of the beam; 2nd, suspension of the lever just above its centre of gravity; and 3rd, care that the friction at the points of suspension both of the beam and of the scale-pans be reduced to a minimum. The points of support in sensitive balances are usually made of fine edges of hardened steel, or of agate, which bear against flat polished plates of agate. Provided that the suspensions be sufficiently fine, it is easy, by the process of *double weighing*, to obtain exact weighings by means of a balance the arms of which are not equal. For this purpose, the material to be weighed is accurately balanced with shot, sand, or any other convenient substance; it is then removed from the pan, and weights substituted, until the sand or shot remaining in the other pan is again accurately counterpoised: the number of weights needed will show the weight of the substance under experiment. In all exact experiments the balance must be screened from currents of air, and the bodies weighed should not be touched directly with the warm hand, as they ought to have sensibly the same temperature as that of the surrounding atmosphere, otherwise currents of air, ascending or descending within the balance case, will be produced, and they will impair the accuracy of the observation. A good balance will indicate a difference of weight equal to about $\frac{1}{100000}$ of what it will carry in each pan.

Density.

(20) If equal volumes of matter of different kinds be compared together, they will be found to differ very greatly in weight:—

At 0° C. Bar. 760mm.		Grammes.
1 litre of hydrogen	will be	0·089578
„ of air	„	1·293187
„ of water	„	999·88
„ of iron	„	7854·
„ of platinum	„	21500·

		Grammes.
or 11·16345 litres of hydrogen	will be	1
„ of air	„	14·43643
„ of water	„	11161·11
„ of iron	„	87677·72
„ of platinum	„	240014·2

Platinum, the densest body with which we are acquainted, is at the standard temperature and pressure upwards of 240,000 times denser than hydrogen, which is the least dense material known.

The comparison of the weights of equal volumes of different bodies, when referred to the same standard, constitutes their density.* The density of a body forms one of its most important and distinguishing physical characters. The mineral iron pyrites, for instance, is in colour almost exactly like gold; but it is at once distinguished from the precious metal by the difference in density, an equal volume of gold being nearly four times as heavy. The numbers used to represent the density of solids or liquids are obtained by comparing a known weight of the body under experiment, with the weight of an equal volume of distilled water, which has been selected as the standard of reference. In this country the experiment is generally made at a temperature of 60° F. For gases and vapours, atmospheric air at 60°, while the barometer stands at 30 inches, is employed as the standard. Unfortunately the standard temperature and pressure adopted in England differs from that employed in nearly every other country. Almost all foreign writers on science adopt the French plan, by which 0° C. (32° F.) is made the standard temperature; and 760 millimetres, or 29·922 inches, the height of the barometer which is assumed as the standard pressure. The unit of density, however, is the weight of an equal volume of water, not at 0° C., but at 4° C., or 39°·2 F., the point of maximum density of this liquid (143).

These relations are more complex than those adopted in

* The *density* of a body is defined as the *mass* contained in a unit of its volume; whilst its *specific gravity* is the *weight* of a unit of its volume.

England; though in the case of liquids and gases there is an advantage in the facility of securing a uniform temperature of 32° at all times by the use of melting ice.

For the purpose of calculating the density of any substance, solid or liquid, it is simply necessary to ascertain, first, the weight of the body in question, then that of an equal volume of water. When this is done, we obtain by simple proportion the density of the body under examination, that of water being assumed as 1. If, as is the case with a large number of solids, they are denser than water, the density merely tells how many times denser they are than that liquid—

Weight of equal volume of water.	:	Weight of body in air.	::	Density of water. 1·000	:	Density required.

(21) *Density of Liquids and Gases.*—The determination of the weights of equal volumes of any liquid and of water is easily made in the following manner:—Take a light bottle furnished with a stopper, and weigh it when empty: fill it with water, and weigh it again; the difference of course will be the weight of the water which it contains. Empty the bottle, rinse it out with a little of the liquid for trial, then fill it with the liquid, and weigh. On deducting the weight of the bottle, we obtain the weight of a volume of liquid exactly equal to that of the water. In practice it is convenient to employ a bottle that holds exactly 10 grammes of distilled water at 4° C., because when such a bottle is filled with the liquid under trial, the weight in centigrammes of the liquid taken at 0° C. represents the density at once, without calculation. For convenience, a counterpoise of brass is adjusted to the weight of the empty bottle. Suppose the counterpoised bottle, which when filled with water weighs 10 grammes in addition to the counterpoise, to be filled with pure alcohol: it will now weigh only 7·92 grammes, and the density of the alcohol will be 0·792; for 10 : 1·000 :: 7·92 : 0·792. The same bottle filled with oil of vitriol would weigh 18·45 grammes. Its density would therefore be represented as 1·845.

FIG. 4.

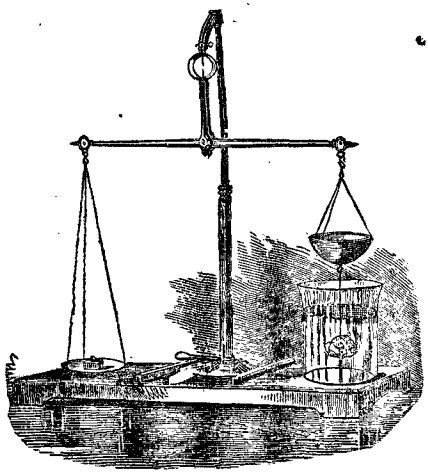
For accurate purposes, a flask of the annexed form (fig. 4) is preferable to all others; a mark at *a*, in the contracted portion of the neck, indicates the level occupied by 10 grammes of water at 4° C. The flask filled with the liquid under trial, a little above this mark, is then placed for an hour in melting ice. At the end of that time the superfluous liquid in the flask is drawn off by means of a pipette till it stands exactly at the level of the mark; the stopper is inserted,

and the weight, after careful drying of the outside, is taken. Bottles which contain 20 or 50 grammes up to the graduation on the neck may be employed instead of the smaller one when the quantity of liquid is large.

The determination of the density of gases is the same in principle; a flask or globe is weighed when empty, again when filled with air, and a third time when the gas under trial has been substituted for atmospheric air. Gases, however, are liable to considerable changes of volume from slight variations of external circumstances; hence, in taking their density, certain precautions are necessary, which will be fully described further on (146).

(22) *Density of Solids.*—With solids, a different, but not less simple method is adopted, though resting on a principle by no means so obvious. This principle was one of the great discoveries of Archimedes: it may be thus explained:—When a body is plunged beneath the surface of a liquid, it obviously displaces a volume of such liquid equal to itself, and consequently it is pressed upon or supported in the liquid, with a force exactly equal to that with which the particles of the liquid were supported, when they previously occupied its place; the solid will therefore appear to have lost weight exactly equal to that of the volume of liquid which it has displaced. The operation required for ascertaining the density consists, therefore, in weighing the solid in air, then having, as in fig. 5, suspended it by a horsehair from the scale-pan, placing it in distilled water,* and again weighing; the difference of the two weights will be that of its own volume of water.

Fig. 5.



* In exact experiments the temperature of the water should be noted, 4° C. being that to which such comparisons are referred, though the temperature of 60° F. (15°·5 C.), hitherto used in England, is practically more convenient, because more easily attained.

A piece of lead, for instance, weighs in air . 8·20 grammes.
" " " in water . 7·49 grammes.

Loss: being the weight of an equal volume of water . . . . . 0·71 grammes.

The density of the lead is obtained from these data by the application of proportion, in the following manner:—

0·71 : 8·20 : : 1·000 : x (=11·549), sp. gr. of lead.

The rule for obtaining the density of a solid may therefore be expressed in the following terms:—Divide the weight of the body in air by the loss which it experiences when weighed in water; the quotient is the required density. The experimental proof of the correctness of the principle—viz., that the solid loses weight equal to that of the water which it displaces, is easily given. Take a solid metallic cylinder which accurately fits, and completely fills, the cavity of a cylindrical cup; counterpoise the two when suspended in air from one extremity of the balance beam. Then withdraw the metallic cylinder, and suspend it by a hair to a hook at the bottom of the cup, which must still remain attached to the balance, and place the cylinder so suspended in distilled water; the counterpoise will now be much too heavy: fill the cup with water—(add, that is, the weight of a volume of water equal to the volume of the cylinder,) and the equipoise will be restored.

Occasionally it happens that a knowledge of the density of a body in the form of a powder is required; in such a case the method of taking the density requires to be slightly modified. Suppose that it be desired to find the density of a species of sand; we may proceed as follows:—Take a bottle which contains, when full, a known weight of distilled water, 100 grammes for example; weigh into it, when empty, a quantity, *e.g.*, 15 grammes, of sand. Supposing that the sand had not displaced any water, the bottle, when filled up with that liquid, would now weigh 115 grms.; but on actually weighing the bottle after it has been filled up, it is found that the water and sand together weigh only 109·6 grms.; the sand therefore has displaced 5·4 grms. of water. We have thus the data for calculating the density of the sand, as follows:—

5·4 : 15·0 : : 1·000 : x (= 2·777), the density of the sand.

If the substance be soluble in water, it must be weighed in air as usual; then in spirits of wine, in oil of turpentin, or in some liquid which does not dissolve it, and the density of which is known.

If the body be so light as to float in water, it must be first weighed in air, and then attached to a solid, the weight of which in water has been ascertained, and which is sufficiently heavy to keep the lighter body, when fastened to it, beneath the surface; the weight in water of the two united bodies is then determined, and the result thus obtained is deducted from the weight of the heavier

solid in water: if to this remainder the weight of the light body in air be added, we are furnished with the weight of a volume of water equal to that of the lighter solid, and have the data for calculating the density by proportion, in the usual manner.

(23) *The Hydrometer.*—Another method of taking the density of liquids consists in the use of the instrument called the *hydrometer* or *areometer.** The hydrometer (fig. 6) consists of a graduated stem, which is made to float vertically in the liquid, by means of a hollow ball of glass or brass counterpoised by a duly adjusted weight attached to the lower end of the instrument. A portion of the stem of the instrument must always float above the surface of the liquid the density of which is to be determined. It is obvious, that when placed in any liquid contained in a vessel of sufficient depth, it will sink until it has displaced a volume of liquid equal to its own weight: in a dense liquid it will sink to a smaller depth, in a less dense liquid it will sink to a greater extent; an additional portion of the stem being in the latter case immersed, until it has displaced a sufficient additional quantity of the liquid to compensate for the diminished density of the liquid under trial. The instrument may either be supplied with a scale graduated upon the stem by trial in liquids of known density, so as to give the result by mere inspection, or an arbitrary scale of equal parts may be used, and the values indicated may be ascertained by reference to tables constructed for the purpose. In practice, it is found convenient to employ two instruments, one of which is graduated for liquids less dense than water, the other for those which are denser; the need of an inconvenient length of stem is thus obviated.

Fig. 6.

The hydrometer is, with suitable precautions, capable of affording very accurate results. A particular form of the instru-

* The term hydrometer means water or liquid measurer, from ὕδωρ, water, and μέτρον, a measure; areometer is derived from ἀραιὸς, rare, and μέτρον. Tables of Baumé's and Twaddell's hydrometers will be found in the Appendix to this volume. Baumé's scale for liquids denser than water is obtained by placing the instrument in distilled water, in which it should sink till the tube is nearly covered. An aqueous solution of sodic chloride, containing 15 per cent. of the dry salt, is then prepared, and the height at which the instrument stands in this solution is marked on the stem; the interval between that and the level for distilled water is divided into 15 equal parts (points), and the remainder of the stem is graduated into degrees of equal value. The strongest oil of vitriol of commerce marks usually about 66° of such an instrument.

ment, known as *Sikes's* hydrometer, is employed by the Excise for determining the strength of spirituous liquors. The ordinary glass instruments, however, only furnish approximations to the truth, which are quickly obtained, and for the common purposes of the arts are sufficiently exact.

(24) *Correction for Weighings taken in Air.*—The apparent weight of every substance in the atmosphere (that is, the attraction with which it appears to be drawn to the earth), is always a little less than its actual weight, because the air presses upon and supports the body with the same force with which it would support a portion of air of the same volume as the body itself. The weight of this displaced portion of air may be easily ascertained, if the density of the body be known: for from the observed weight of the body, we can calculate directly the weight of an equal volume of water, and $\frac{1}{816}$ of this weight will give the weight of a corresponding volume of air at $15^{\circ}\cdot5$ C. and $760^{mm.}$ barometric pressure, or $\frac{1}{773}$ at 0° C. under the same pressure. This weight must be added to that actually found; at the same time a similar and opposite correction will be required for the metallic weights used in the experiment, because they will also appear to be lighter than they really are; and an amount of weight greater than the true one will be required to effect the counterpoise. If, therefore, the weights have the same density as the body counterpoised, the two corrections will neutralize each other; but if, as in weighing gases, there is a great difference between them, the correction will be one of importance. The true weight sought will be thus obtained:—Add to the weight of the body in air, the weight of the volume of air which it has displaced, and deduct from this the weight of the volume of air displaced by the weights employed.

The correctness of the foregoing observations admits of an easy experimental illustration. If a light body, such as a piece of cork, be suspended in air from one end of a scale-beam, and be counterpoised at the other end by a metallic weight, then on placing the apparatus under the receiver of the air-pump, and exhausting the air, the cork will gradually acquire the preponderance; but on again admitting the air, the equilibrium will be restored.

CHAPTER III.

ON SOME VARIETIES OF MOLECULAR ACTION.

I. *Elasticity.*—II. *Cohesion.*—III. *Adhesion.*—IV. *Crystallization.*

(25) Besides gravity, which operates through distances so vast that the mind is lost in the attempt to estimate and explore them, other forms of attraction exist; but they are exerted only through distances so minute, as to be inappreciable to our unaided senses: and yet, upon the exertion of these attractions, the form, and even the chemical properties of bodies depend.

The first of these actions is known as *cohesion;* it acts between the particles of matter which are similar in kind. The degree of intensity with which this attraction is exerted in each

particular case determines whether the body be solid, liquid, or gaseous.

The second of these actions is that of *adhesion;* it is exerted between portions of matter dissimilar in kind, and unites them, as in the case of the intervention of cements, into one consistent whole.

The third, and to the chemist the most important, is that known as *chemical attraction,* which causes the union of dissimilar particles of matter of invisible minuteness, rearranges these particles in new forms, and produces a compound body endowed with new properties.

Reacting against all these molecular attractions, is the repulsion of *heat,* which may be raised high enough to overcome them all, and which in a modified form, when balanced against these attractions, produces that equipoise in distance between the constituent particles of material objects in general, which is designated as *elasticity.*

Attractions which thus act at these minute distances only, are termed *molecular* actions, in contradistinction to those which, like gravity, act upon the mass, and operate through great distances.

§ I. Elasticity—mechanical properties of gases.

(26) By *elasticity* we understand the resistance that a body offers to compression or to extension, and the property which it possesses of regaining its form or volume when the pressure or tension is withdrawn.

The law which regulates elasticity, in perfectly elastic bodies, may be expressed by the statement that the strain (elongation or compression) produced by the application of an external stress is proportional to the stress. Most ordinary solid bodies are sensibly perfect in elasticity when the stress applied does not exceed a certain limit. For example, a bow, or a spring bent to a certain extent with a tension of 10 lb., will be bent to double that extent with a tension of 20 lb.

All solids have limits to their elasticity, and there are very few which are perfectly elastic, even within those limits; that is to say, there are few solids which recover their form perfectly after having been stretched or compressed; if compressed beyond a certain point, they either 'set,' and alter their shape, as is the case with lead; or they break, as is the case with glass. The elasticity of glass and steel is, within the bounds of their cohesion, almost perfect: that of caoutchouc, on the contrary, is imperfect; for, by frequent stretching, it becomes permanently elongated.

When a rod is stretched within the limits of its elasticity, the extension is proportional to the tension applied: a tension produced by a weight of 2 kilos. will produce an extension double of that produced by 1 kilo. For equal weights,

the elongation is proportioned to the length of the rod: a wire 1 metre in length will be stretched twice as far by a weight of 1 kilogramme as a piece of the same wire only half a metre long.

Liquids possess a very perfect elasticity, which varies in amount in different liquids; the densest liquids, in general, being those which least admit of compression, *i.e.*, possess the greatest coefficient of elasticity. The following table exhibits some experimental results obtained on this subject by Colladon and Sturm (*Ann. Chim. Phys.* 1827 [2], xxxvi. 113, 225).

Compressibility of Liquids.

Liquid used.	Density. Water = 1.	Temp. ° C.	Mean cubical compression in millionths for each additional atmosphere.	Range of pressure in atmospheres.	Variations in compressibility.
Mercury	13·596 at 0°	0°	5·03	1 to 30	regular
Sulphuric acid ...	1·845 ,,	,,	32·0	1 ,, 16	,,
Water	1·000 ,,	,,	51·3	1 ,, 24	,,
Acetic Ether ...	·910 ,,	,,	76·0	1 ,, 16	79 to 71
Oil of Turpentine	·87 ,,	,,	73·0	1 ,, 26	regular
Hydrochloric Ether	·920 ,,	11°	84·0	1 ,, 12	85·9 to 82·2
Alcohol	·800 at 11°	,,	93·5	1 ,, 24	96·2 ,, 89
Ether	·736 at 0°	,,	145·0	1 ,, 24	150 ,, 141

One million parts of mercury, for example, were found, by each additional pressure of 1·033 kilogrammes per square centimetre, or of about 15 pounds upon the square inch, to diminish in volume 5·03 parts. One million parts of water suffered a compression ten times as great, being reduced more than 51 parts; the pressure of the atmosphere being estimated on an average at 1.033 kilo. per square centimetre, or about 15 pounds weight upon every square inch of the earth's surface.

Regnault has more recently determined the compressibility both of water and of mercury with very great care. He considers the results of Colladon and Sturm to be a little too high; and estimates the diminution in the volume of mercury for each atmosphere at 3·5 millionths of its volume; whilst he found that of water to be equal to 47 millionths of its volume.

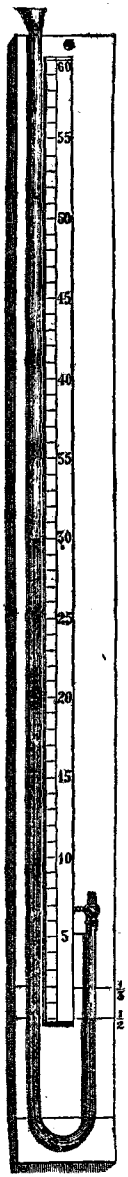
The compressibility of water is greater at low than at high temperatures; but according to the experiments of Grassi (*Ann. Chim. Phys.* 1851 [3], xxxi. 477) the compressibility of ether, alcohol, and chloroform is increased by elevation of temperature; and in the case of these liquids, and notably in that of wood spirit, the compressibility increased with the pressure within the range of his trials, which, however, did not exceed 9 atmospheres.

Andrews has lately shown that liquid carbonic anhydride is much more compressible than ordinary liquids.

(27) *Boyle's or Mariotte's Law of Elasticity in Gases.*—It is, however, in gases that the most extensive and perfect display of elasticity is to be seen; their great elasticity constitutes indeed their most important physical peculiarity. It may be stated, without sensible error, that within the limits of ordinary experiment, 'the volume of an aëriform body is inversely as the pressure to which it is exposed;' consequently by doubling the pressure we halve the volume, by trebling it we reduce it to one-third;

'but the elasticity is increased directly as the pressure;' by doubling the pressure we double the elasticity. These facts are strikingly exhibited in the following experiment devised by Boyle, and more accurately performed by Mariotte; and the law has hence been termed Boyle's or Mariotte's law:—

FIG. 7.



Take a bent tube (fig. 7) of uniform bore, one limb of which is about 12 inches or 30 centimetres long, and furnished with a stop-cock; the other limb being 6 feet, or about 2 metres, in length, and open at the top. Pour a little mercury into the bend of the tube, and close the stop-cock. The air in the short limb now has the same elasticity as the atmosphere at the spot; and the air at the surface of the earth, as will presently be more fully explained, is under the pressure due to the weight of its own superincumbent mass; the amount of this pressure is ascertained by observing the height of the mercurial column in the barometer at the time. Next pour mercury into the open limb of the bent tube; the air in the shorter limb will slowly diminish in volume: when the mercury in the longer limb stands above the level of that in the shorter, at a height exactly equal to the height of the barometer at the time, say 29·92 inches ($760^{mm.}$), the compressed air will occupy a length of the shorter tube exactly equal to one-half of that which it did at the beginning of the experiment; the air is subject to a pressure exactly double. On adding more mercury, till the length of the column in the long tube, above the level of that in the shorter, is equal to twice the height of the barometric column, the pressure will be increased threefold, and the air will now occupy only one-third of its original volume.*

* The researches of Despretz, and the more recent and elaborate experiments of Regnault have, however, shown that this law is not rigidly accurate, but it is what is termed a *limited law*, as it fails in extreme cases. For atmospheric air, for hydrogen, oxygen, and nitrogen, and generally for gases which have either never been liquefied, or only liquefied under enormous pressures, the law is very nearly correct, even under a pressure of several atmospheres: but for gases which may be liquefied more readily it is not so; the nearer they are made to approach to the point of liquefaction the greater is the difference between the volume actually observed, and the

(28) *Mutual Repulsion of the Particles of Gases.*—Gases and vapours, or *elastic fluids*, as they are frequently termed, differ from liquids in the entire absence of cohesion among their particles. A vessel may be filled either partially or completely with a liquid, and this liquid will have a definite level surface or limit. With gases it is otherwise; they always perfectly fill the vessel that contains them, however irregular its form. Instead of cohesion there is a mutual repulsion among their particles. These particles have a continual tendency to recede further from each other, and they therefore exert a pressure in an outward direction upon the sides of the vessel which contains them. This outward pressure is greater or less according as the pressure of the gas is increased or diminished. Indeed, the volume of a gas depends entirely upon the pressure. These facts admit of experimental proof in the following way:—

FIG. 8.

Procure a stout cylindrical glass tube open at one extremity, and capable of being closed at the other by a stop-cock; fit it with a solid plunger that slides air-tight up and down within it; open the stop-cock, place the plunger half-way down, and fill the vessel with some coloured gas, such as chlorine, for example, as shown in fig. 8; now close the stop-cock, and draw the piston upwards, the gas will be seen to dilate, and the green vapour will still entirely fill the tube; but a considerable resistance to

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result calculated. The contraction is nearly always found to be more considerable by experiment, than it should be by the law usually assumed (197).

Some of the results obtained by Regnault are embodied in the following table; they show considerable deviations from the law in four important gases under high pressures.

Relative Volumes of Gases at High Pressure.

Relative volumes of Gas.	Pressure in Atmospheres in the case of			
	Air.	Nitrogen.	Carbonic Anhydride.	Hydrogen.
1	1·000000	1·000000	1·000000	1·000000
·1	9·916220	9·943590	9·226200	10·056070
·05	19·719880	19·788580	16·705400	20·268720

The elasticity of hydrogen therefore increases even *more rapidly* than the pressure; with the other gases the elasticity does not quite keep pace with it. It would seem from these experiments as if there were more probability of liquefying oxygen than nitrogen, and both these than hydrogen.

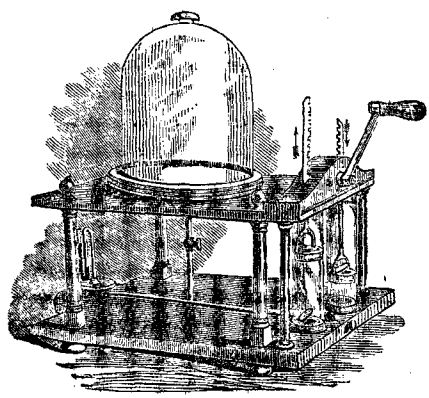
the upward motion of the piston is experienced, the dilated gas has its pressure reduced below that of the external air, and on releasing the handle, the piston is forced back to the middle of the tube; the pressure of the gas within, and that of the air without, are now equal. Now attempt to thrust the piston to the bottom of the tube; great resistance will be experienced, but the gas will yield and will be condensed into a smaller space, while its pressure will be proportionately increased; but the instant that the pressure on the piston is removed, the piston will rise up again, and occupy its first position midway between the two ends of the cylinder.

(29) *Air-Pump.*—Advantage is taken of this elasticity and expansibility of gases in the construction of the air-pump, an instrument designed for the removal of air from closed vessels. The principle of its construction may be explained in the following manner:—

FIG. 9.

Suppose that a metallic cylinder, accurately bored, be fitted with a piston similar to that shown in fig. 8, but provided in addition with a small opening, covered by a flap or valve of oiled silk, which opens upwards or outwards (fig. 9): on forcing the piston downwards the compressed air will escape through the valve, but on attempting to withdraw the piston no air will be able to re-enter the cylinder, and a resistance will be experienced, owing to the pressure on the upper surface of the piston occasioned by the pressure of the external air. If the cylinder be provided with a second valve at the bottom, opening in the same direction as that in the piston, this valve will, on thrusting down the piston, be closed by the pressure of the included air, while the upper valve will be opened; on withdrawing the piston the effect is reversed, the lower valve rises, and the air enters, while the valve in the piston is firmly closed. Such an arrangement constitutes the *exhausting syringe* or air-pump in its simplest form. In the usual and more convenient form of the air-pump (fig. 10), a brass tube passes from the bottom of the syringe and terminates

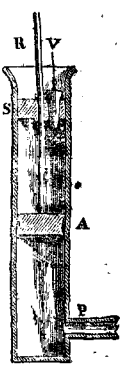
FIG. 10.



in the centre of a disk of brass or of glass, ground accurately flat; the vessel from which the air is to be exhausted also has its edge ground truly, and it is inverted upon the plate. On elevating the piston, the pressure of the air within the vessel or receiver raises the lower valve, and the dilated air enters the vacuum produced in the lower part of the cylinder by the withdrawal of the piston; the air thus admitted, again raises the valve of the piston, when the latter is so far depressed as to render the pressure of the air beneath it greater than that of the atmosphere: the same action goes on with every successive motion of the piston, until the pressure of the air within becomes so much diminished as to be insufficient to raise the lower valve. For convenience, two of these exhausting syringes are often combined in the air-pump, and are made to work alternately by a rack and pinion.

(30) *Air-Pump with Single Barrel.*—A more complete vacuum may be obtained with a pump of simpler construction, but the labour of using it is considerably greater. The difference between this form of the instrument and the one just described will be readily understood with the assistance of fig. 11. This pump consists of a single barrel, within which a solid plunger, A, moves air-tight. The plunger is connected with a smooth solid rod, R, which also works air-tight through a stuffing-box, S, at the top of the barrel. In the head of the cylinder is a conical metallic plug, or valve, V, opening upwards and projecting a little way below the under surface of the head, which is ground flat. The communication, P, between the plate of the pump and the barrel, is made at a sufficient distance from the bottom to allow the plunger to pass completely beyond it. In order to use the instrument, the plunger is carried down to the bottom of the barrel, the receiver is then attached to the plate, and the piston raised. In rising, the air contained in the barrel is expelled through the valve in the cylinder head, and bubbles up through the oil placed there to keep the joints air-tight. When the piston now descends, a complete vacuum is formed above it, until it passes below the aperture which leads to the receiver; the air then rushes in above the piston; this portion is in turn expelled by raising the piston again; and the exhaustion may in this way be carried on till it becomes almost complete, because the valve is now raised not simply by the elastic force of the air confined between it and the piston, but it is pushed up by the upper surface of the piston itself, and the last bubble of air is displaced by a drop of oil which flows past the valve and thus effects its expulsion.

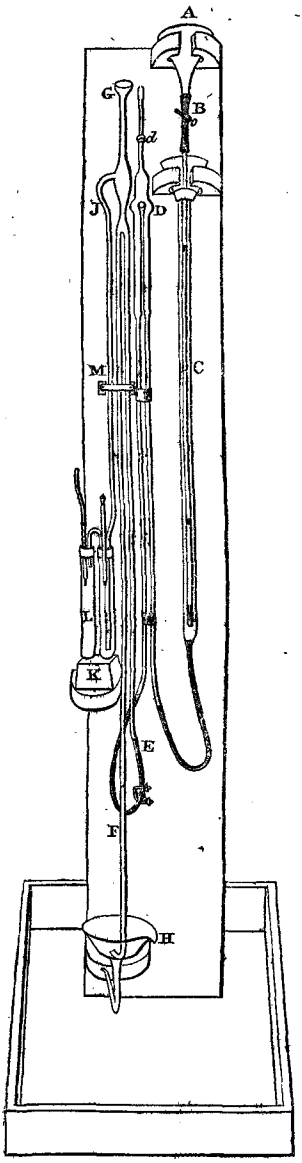
FIG. 11.



(30 *a*.) *Sprengel's Mercurial Air-Pump.*—A very ingenious and valuable instrument has been described by Dr. Sprengel. (*Journ. Chem. Soc.* 1865 [2], iii. 9), by which a very high degree of rarefaction may be obtained. The pump is based on the same principle as that of the blowing apparatus of the Catalan forge—viz., the carrying of a stream of gas down a tube by the fall of a liquid. The simplest form of the Sprengel that was first described is shown in fig. 44 (70); in this apparatus, the mercury from the funnel in falling past the branch tube incloses bubbles of air, which are carried down the tube and delivered at

the orifice under the mercury in the vessel at the bottom. Many alterations have since been made in the shape of the apparatus, and that shown in fig. 11 *a*, has been found very convenient. The mercury is supplied by the funnel, A, the flow being regulated by the compression-cock, B, from which it descends through a narrow tube hanging loosely in a wider tube, C, any air bubbles that may be carried down the narrow tube escape through the annular space between the two tubes. From C the mercury traverses a caoutchouc tube covered with canvas or tape into the air-trap, D (the action of which will be described directly), from this it again descends, and, by means of another covered caoutchouc tube, is conducted into the tube, E, through which it rises to supply the fall-tube, F, which is the active portion of the pump. The vertical distance between the lower end of C and the bend of the air-trap, D, must not be less than 800$^{mm.}$ When the apparatus is first filled with mercury, the compression-cock on the second caoutchouc tube is closed, the stopper, *d*, at the top of the air-trap removed, and the mercury allowed to flow gradually through B, until the air is entirely expelled from the air-trap, which is facilitated by removing the latter from the screw on which it rests, and lowering it until the mercury reaches the orifice, *d*, when the stopper is replaced and the air-trap again suspended from the screw. The lower compression-cock may now be opened, which permits the mercury to rise in E, and enter the top of the fall-tube. When the tubes are of the proper diameter (about 1$^{mm.}$), and the bend at the top of the fall-tube rightly constructed, the mercury passes down the fall-tube in separate drops, forming pistons of equal length, and carrying the gas down quite regularly. The receiver to be exhausted is connected by a glass ball and socket-joint, or otherwise, to the tube, G; and the gas pumped out is delivered through the mercury in the funnel, H. After the pump has been at work for some time, the fall-tube is liable to become soiled, which much interferes with the efficient action of the apparatus. The tube may be cleaned by the introduction of concentrated sulphuric acid, which can be admitted through the tube, J, the lower end of which passes through the cork of a wide tube containing mercury, covered with a layer of sulphuric acid; to introduce the acid, the block, K, is removed, and the wide

FIG. 11 *a*.



tubes lowered until the end of J is above the mercury, the acid then passes up the tube into the pump. The second tube, L, contains sulphuric acid, to dry the air before it comes in contact with that which is to be used for the pump. The funnel, H, is arranged to deliver mercury from the narrow bent tube attached to it, the sulphuric acid passing over the lip. When the pressure in the receiver is reduced to about $50^{min.}$ a vacuum is formed in the air-trap, D, and the mercury thus falls through a vacuum before reaching the fall-tube, any air which may be dissolved in the mercury is thus given up in the trap, and not into the receiver. By using caoutchouc connexions at the bottom of the apparatus, rigidity is avoided, which is of great value when fitting up the pump, the fall-tube merely rests in the funnel, being held upright by a loose support at M. There is no danger of leakage of air through the caoutchouc, since there is always a considerable internal pressure of mercury, and air cannot possibly penetrate into the receiver if the supply funnel becomes empty, for the difference of level between the mercury in the bend of D and in the tube C, cannot exceed the length of the barometric column. By means of an instrument similar to this, Mr. W. F. Donkin has obtained some very perfect exhaustions (*Chem. News*, 1874, xxix. 125). Without the air-trap, and by connecting the receiver to the pump by an india-rubber joint surrounded by glycerine, the pressure was reduced to $\frac{1}{10770000}$ of that of the atmosphere. When the air-trap was employed, and the receiver hermetically sealed on to the pump, the best exhaustion obtained was $\frac{1}{93792000}$ of the atmospheric pressure.

(31) *Pressure of Air.*—The increase in volume of the inclosed air, and consequent decrease in its pressure, may be illustrated by inserting a tube, blown into a bulb at one end, full of air, and with its open mouth downwards in a vessel containing water, which is placed under the receiver of the pump. With each movement of the piston, the air in the bulb expands, while a portion of it in the act of expanding escapes, and bubbles up through the water. An amusing variation of this experiment may be made by placing a number of shrivelled apples in the receiver, and then working the pump. The apples contain air in their pores, which is prevented from escaping by the rind; on working the pump the diminished pressure causes this imprisoned air to expand; in consequence, the apples swell up, and regain their fresh and plump appearance. The illusion vanishes the moment the atmospheric air is readmitted, because the pressure of the external air reduces that in the apples to its former bulk. The pressure thus exhibited is very considerable, as may be shown by the following experiment. Take a thin vessel, such as a light flask, and seal it up full of air; now if the air be exhausted from a receiver placed over it, the flask will be burst into fragments. The great pressure which air exerts against the internal surface of the vessels in which it is contained, may also be exhibited by allowing a weight of several pounds to rest upon a bladder placed under the receiver of the air-pump; on exhausting the air from the receiver, the air in the bladder expands, and lifts the weight.

(32) *Condensing Syringe.*—If the valves in the syringe be made to open in the direction opposite to those of the air-pump, the instrument constitutes the *condensing syringe.* By attaching it to a reservoir capable of resisting the pressure, as shown in fig 12, air may be compressed without difficulty, and stored up as a mechanical power; the pressure of air so compressed is

FIG. 12.

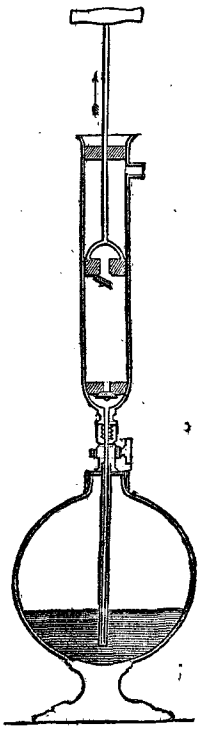
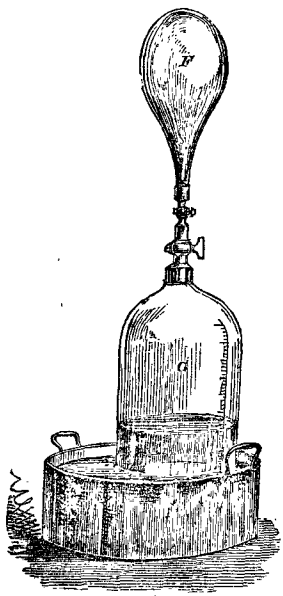


FIG. 13.



capable of being brought suddenly into exercise. Instances of this kind are furnished in the compressed air-fountain, and in the common forcing-pump, one variety of which constitutes that invaluable machine, the fire-engine. A still more striking illustration is seen in the air-gun, where the power of compressed air is made to execute the office of ordinary gunpowder, a substance which may be regarded as a magazine of condensed air which can be brought into action at will.

(33) *Weight of the Air.*—By means of the air-pump it is easy to show by direct experiment, that air, in common with every form of matter, has weight, and even to measure its weight. For

this purpose a well-shaped globular flask, F, fig. 13, furnished with a small stop-cock, is screwed to the plate of the pump, and the air is exhausted. In this state it is transferred to a good balance and accurately counterpoised; it is then attached to a graduated jar, G, filled with air, also provided with a stop-cock, and standing over water; the moment that, by opening the stop-cocks, a communication is made between the jar and the flask, the air rushes into the exhausted vessel. The amount that thus enters is read off by noticing the level of the water before the stop-cocks are opened, and then estimating its rise afterwards by the marks on the side of the jar. On transferring the flask back to the balance, it will be found to have increased in weight several grains.

Minute attention to a variety of circumstances is required to insure a correct result in this experiment. It is by experiments conducted on this principle that the density of the air has been well ascertained (146).

According to Prout, 100 cubic inches of air at a temperature of 60° F., when the column of mercury in the barometer stands at 30 inches, are 31·0117 grains. Regnault found that 1 litre of air at 0° C., was (barometer 760^{mm}, also at 0° C.) 1·293187 grammes. This, if reduced to the English standards, would make the 100 cubic inches of air amount to 30·938 grains,* or 13 cubic feet of air would be about 1 lb.

We may form some notion of the density of the air, by calculating the quantity contained in a given space. Take, for example, a room 10 metres square, and 5 metres in height, offering a cubic content of 500 cubic metres: since a litre of air is 1·293187 grammes, a cubic metre, or 1000 litres, will be 1·293187 kilogrammes, and 500 cub. metres of air will be 646 kilos. Such a room in English measures would be about

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* According to Regnault, the density of mercury at 0° C. is 13·596, water at 4° C. being taken as 1; consequently the relative densities of air, water, and mercury will be—

Air at 0° C.		Water at 4° C.		Mercury at 0° C.
1	:	773·3	:	10513·5

under a barometric pressure of 760^{mm}, or 29·922 English inches at 0° C. Calculating these values all at the temperature of 60° F., and at the barometric pressure of 30 inches, the mercurial column being also at 60° F., and allowing for the relative expansion of water and mercury by heat, the ratios will be the ollowing—

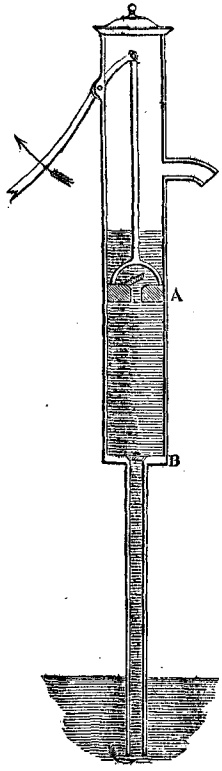
Air,		Water,		Mercury,
1	:	816·62	:	11082

32·809 feet square, and 16·4045 feet high, with a cubic content of 17658·3 cub. feet, and the air that it contains at 60° F. and 30 in. barometer, would be about 1349 lb. or 12 cwt.

It is obvious that if, in the experiment with the flask, just described, the graduated jar had contained any other gas instead of atmospheric air, it would be possible to ascertain the weight of a given quantity of such gas; and by comparing this weight with that of an equal volume of air, to ascertain its density.

(34) *Household Pump.*—The air is the power which raises water in the bore of an ordinary pump. The construction of this very useful machine will be at once understood from the description of the air-pump which has been already given; the arrangement of the valves being similar. Suppose that at first there is no water in the body of the pump. On depressing the piston rod (fig. 14), air escapes through the upper valve, A, and on raising it again, a fresh portion enters from the pipe attached below the second valve, B. The pressure of the atmosphere upon the surface of the water in the well forces up a portion of this liquid till it reaches a height at which the pressure due to the column raised together with the diminished pressure of the air in the barrel is equal to that of the atmosphere; on again depressing and raising the piston several times successively, the whole of the air at length has its place supplied by the water thus raised from the well below, the pressure of the atmosphere being partly removed from the surface of the water contained in the pipe beneath the valves. It is manifest, however, that there must be a limit in the height to which water can be raised in this way. As soon as the column of water in the pump above the level of that in the well is long enough to balance the pressure of the air, the water will rise no higher. Such a column of water is about 33 feet, 10·33 metres in height. If a tube 40 feet (or nearly 12 metres) long be closed at its upper end, filled with water, and then placed mouth downwards in a vessel of water, the water in the tube will fall till it stands about 10 metres

Fig. 14.

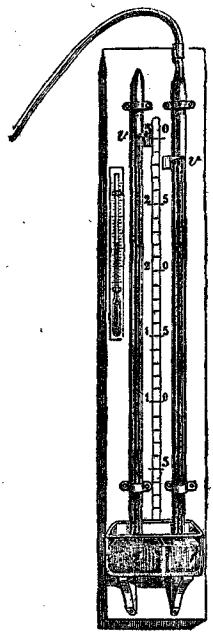


above the level of that in the cistern. Such a tube, forming, in fact, a *water barometer,* was placed by the late Professor Daniell in the hall of the Royal Society. It is very sensitive to changes in the pressure of the atmosphere, the column during a gale of wind rising and falling visibly in the tube.

(35) *Pressure Gauge and Barometer.*—If the tube were filled with a liquid denser than water, a proportionately shorter column of it would be sustained by the pressure of the air, the length of the column being inversely proportional to the density of the two liquids. Now as mercury is rather more than 13 times denser than water, this liquid metal will rise to a height only about $\frac{1}{13}$ as great as that of water, or to a height of about 30 inches (762 millimetres) instead of 10·33 metres. This result is easily verified; for if a glass tube about one metre in length, and closed at one extremity, be completely filled with mercury, the aperture closed with the finger, and it be placed mouth downwards in a basin of mercury,—on removing the finger, the column of fluid metal will partially descend, and leave a void space of 240 or 250 millimetres (about 10 inches) in length in the upper part of the tube. But the most complete demonstration that the mercury is sustained solely by the pressure of the air upon that in the basin, is furnished by placing the whole apparatus under the receiver connected with the air-pump: as the air is exhausted, and consequently the pressure is diminished, the column sinks; but it recovers its former level on readmitting the air from without. A tube, or *air-gauge,* acting on this principle, is usually attached to every air-pump, as a convenient means of judging of the perfection of the vacuum. If it were possible wholly to exhaust the air from the receiver, the mercury would rise in such a gauge (which is simply a tube open at top into the receiver, and dipping below into a basin of mercury) until it stood at the same level as in the barometer at the time of the experiment: but this result is never attained in practice; the pressure of the portion of air remaining in the receiver always depresses the mercury nearly a millimetre in the gauge below this point. By means of the gauge, the density of the air still remaining in the receiver is readily ascertained, for the density is always proportional to the pressure. Suppose, then, the gauge showed a residual pressure of 2 millimetres, the remaining air would have only $\frac{1}{380}$ of the density that it possessed at the commencement, if the atmospheric pressure shown by the barometer at the time were equal to that due to a column of 760 millimetres in height.

Regnault employs a gauge, at the side of which an ordinary

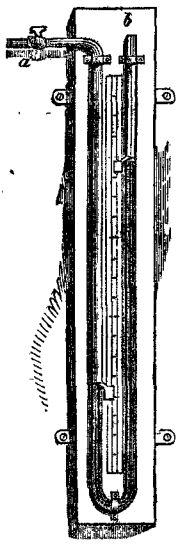
Fig. 15.



mercurial barometer plunging into the same cistern is placed (fig. 15), so that the difference in height between the two columns of mercury may be read off with great accuracy by means of a graduated scale and verniers, *v*, *v*.*

A simple pressure gauge or *manometer* (from μανὸς, rare) for estimating the rarity or condensation of air in a confined space, is made by bending a tube into the form shown in fig. 16, and pouring water into the bend; the apparatus is attached at *a* to the air vessel, the other limb, *b*, being open to the atmosphere; by the difference of level, the pressure of the gas under experiment can be accurately estimated by a scale placed between the tubes. When the pressures are considerable, mercury is used instead of water. A pressure gauge of this simple description is in constant requisition in coal-gas works for estimating the pressure in the gasometer, in the street mains, or at any part of the services.

Fig. 16.

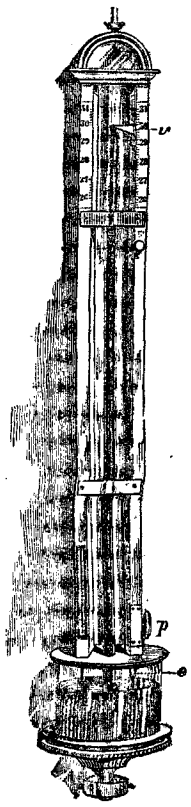


A simple inverted tube when filled with mercury, with due precautions to exclude every particle of air, and furnished with accurate means of measuring the height of the column above the level of the mercury in the cistern, constitutes one of the most indispensable philosophical instruments—the *barometer* (from βάρος, a weight, and μέτρον, a measure). The diameter of the tube is of little consequence; but a tube of from 8 to 13 millimetres ($\frac{1}{3}$ or $\frac{1}{2}$ an inch) wide, or wider, is preferable to one of smaller bore. A slight fixed correction for capillarity, varying with the diameter of the tube, is required for each instrument. In the best instruments of this description the whole scale is moveable by a rack and pinion, *p* (fig. 17), and can be adjusted so that its lower extremity, which for convenience of observation is made to terminate in a fine

* The difference in height may be still more accurately read off, without the

steel point *e*, can be brought to coincide exactly with the surface of the mercury in the cistern: unless this contrivance were adopted, it would not be possible to measure accurately the height of the column of metal, because the level of the mercury in the cistern is continually undergoing slight variations: as the metal rises in the tube it falls in the cistern, and *vice versâ:* part of the cistern is constructed of glass, to allow the point of the scale to be seen. The height of the mercurial column above the level of the mercury in the cistern, when the instrument has been placed in a truly vertical position, is read off at the top by a vernier *v*, which estimates differences of a tenth of a millimetre. The barometer has been constructed in a great variety of forms, but the simple inverted tube is the best for ordinary purposes.*

FIG. 17.

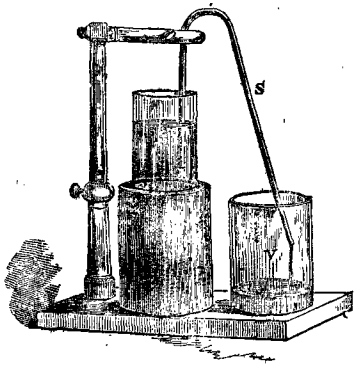


(36) *The Syphon,* which is another instrument in frequent use in the laboratory, depends for its operation partly upon the principle of atmospheric pressure. The syphon is a bent tube, by means of which liquids may be lifted above the level at which they stand, provided that they are ultimately transferred to a lower level. Suppose that it be desired to draw off a liquid without disturbing a powder which has settled down to the bottom of a vessel; a bent tube or syphon (s, fig. 18), one limb of which is longer than the other, is filled with water, and closed by placing the finger at the end of the longer limb; the instrument is then inverted, and the short limb is plunged rapidly into the liquid to be decanted. On removing the finger

employment of verniers, by using an instrument called a *cathetometer* (from κάθετος, a perpendicular), which consists of a telescope of short focus, furnished with a spirit level, by which its horizontality may be secured. Upon a graduated scale, which is placed truly vertical, the telescope slides up and down, and is raised or lowered until its cross-wires coincide with the level of the mercury. With an instrument upon this principle properly constructed, differences in vertical height in the mercurial columns may be determined with minute precision. It is the method uniformly adopted by Regnault.

* A table, giving the values of the barometric pressure in millimetres, expressed in the corresponding number of English inches, will be found at the end of this volume.

Fig. 18.



from the longer limb, the liquid flows, and will continue to do so as long as the shorter limb remains below the surface of the liquid in the vessel. If the vessel v, however, be raised until the longer limb of the syphon is immersed in the liquid that has run over, and the liquid stands at the same level in both vessels, no further flow will take place; if v be again depressed, the flow through the syphon will again be renewed. When, as was effected by the expedient of raising the lower vessel till the liquid stood at the same level in both, the acting limbs of the syphon are of equal length, the column of liquid in each has the same perpendicular height, and the downward pressure of each column will be the same: neither column will preponderate over the other: but if the vertical column of liquid be longer on one side than on the other, this longer column will necessarily press downwards with more force on that side than the column in the shorter limb presses in the opposite direction; the atmospheric pressure, however, is equal on both sides; the heavier column therefore runs out of the tube, drawing with it the liquid in the shorter limb, and the place of this liquid is supplied by a fresh portion from the vessel, owing to the pressure of the atmosphere which drives it up into the space that would otherwise become empty.

(37) *Pressure of the Atmosphere.*—From what has been already stated, it must be obvious that we are living at the bottom of a vast aërial ocean, and subject to the pressure due to the superincumbent mass,—a pressure which amounts to about 15 pounds upon every square inch of surface, and as has been estimated, to about 14 or 15 tons weight upon the surface of the body of a man of average stature.*

The existence of this pressure of the air is a matter of the highest importance to us. It admits of proof by experiment in a variety of ways. The receiver of the air-pump may at first be

* Every square centimetre supports an atmospheric pressure amounting to a little more than the weight of 1 kilogramme, or more exactly 1·033 kilog., when the barometer stands at 760^{mm}, and the surface of a man's body would sustain an average pressure of about 15000 kilogrammes.

lifted from the brass plate without difficulty, but after a few strokes of the pump in the ordinary process of exhausting, it becomes fixed by the pressure of the air, uncompensated by that within the vessel. It is for this reason that an arched form is given to the external surface of vessels designed to bear exhaustion. If the hand be placed over the mouth of a receiver having at the top an opening of 2 or 3 inches (6 or 8 centimetres) in diameter, a very partial removal of the air will make this pressure painfully sensible; and if a piece of bladder be moistened and securely tied over the opening and then left to dry, its surface will, when a portion of the inclosed air is removed, become very tense and concave, and if the exhaustion be carried far enough, it will suddenly burst with a loud report.

But the question will naturally arise, how is it, that if our bodies are subjected to the pressure above indicated, we are not only able to support it without being crushed or rooted to the earth, but are even insensible of its existence. The reason is, that the pressure is equal in all directions. A very simple experiment will suffice to demonstrate the upward pressure. Take a glass jar with a smooth edge (a common wine-glass will do), fill it with water, close the mouth with a card or with a bit of paper, retain the card in its place with the hand, and turn the jar mouth downwards; the hand may be removed, the card will remain supported, and the water will not escape. Indeed we might thus support a column of water 10 metres long (but not longer), as that would just balance the pressure of a column of air of equal diameter. It is the pressure, exerted in all directions on the blood, pervading every tissue of our frame, which renders us unconscious of the atmospheric pressure. If the pressure upon the surface of the body be decreased, as by ascending in a balloon, considerable inconvenience is often experienced; bleeding at the nose, and other unpleasant symptoms sometimes arising, from the diminution of the atmospheric pressure on the surface of the body. Blood flows in the operation of cupping, because the atmospheric pressure is partially removed over the wounds inflicted by the lancets.

(38) *Pneumatic Trough.*—Among the many useful contrivances depending on the pressure of the air, is a simple but valuable apparatus of Priestley's, called the *pneumatic trough*, which enables us to confine air and gases in vessels, and to decant them from one to another with as much ease as liquids may be managed and poured.

The pneumatic trough consists of a vessel containing water, fig. 19, across which, at the depth of from 5 to 8 centimetres from the top, a ledge or shelf is placed; the jars destined to receive the gas are filled with water, and placed with their mouths downwards upon the shelf, which is kept about an inch (2 or 3 centimetres) under water; into these jars the gas is allowed to bubble up, and it may be transferred from one jar to another by an inverted pouring. When a jar has been filled, or partially filled with gas, it may be readily removed from place to place by sliding under its open mouth, while still immersed in water, a plate or shallow tray, containing water, on which it may be lifted out of the pneumatic trough as at B.

FIG. 19.

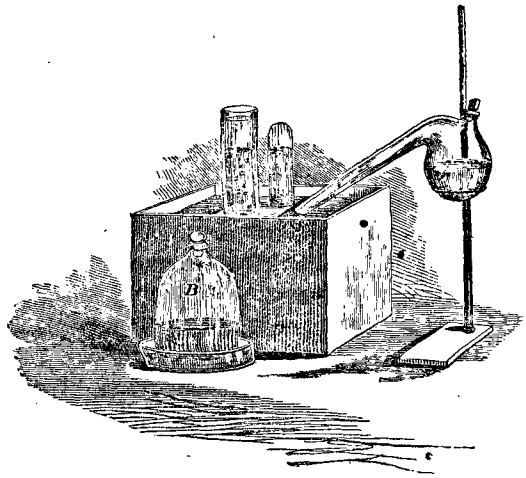
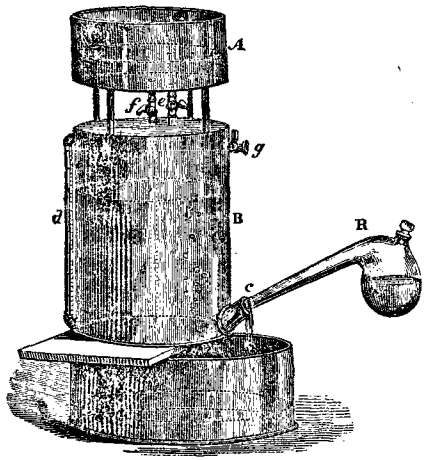


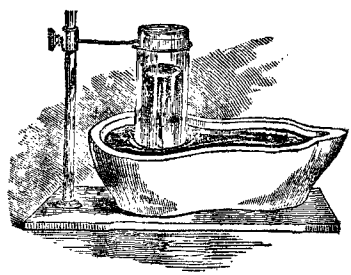
FIG. 20.



(39) *The Gas-holder.*—When large quantities of gas are to be stored up, a different apparatus, the *gas-holder*, is employed, and in this instrument also, advantage is taken of the pressure of the atmosphere. The gas-holder is represented in fig. 20. It consists of a cylinder, B, surmounted by a tray, A, for holding water; this tray communicates with the cylinder by means of two pipes provided with stop-cocks; one of these pipes, *f*, proceeds nearly to the bottom of the cylinder, B, and is open at both extremities; the other pipe, *e*, only just enters the top of the lower cavity: at the lower part of the cylinder is a short wide pipe, *c*, passing obliquely upwards, and furnished with a plug, by which it can be closed at pleasure. A third stop-cock is introduced at the upper part of the cylinder at *g*, to which a flexible tube may be attached for the convenience of transferring the gas. Now suppose the gas-holder to be full of atmospheric air, and to be wanted for use; the pipe, *c*, at the bottom is closed, water is poured into the tray, and both stop-cocks in the vertical pipes are opened: the water descends through the longer pipe, *f*, whilst the air escapes in bubbles through the shorter one, *e*: when B is completely full, the stop-cocks are closed, and the plug at the bottom removed; no water escapes, owing to the pressure

of the atmosphere upon the surface of the liquid in the wide tube, *c*, the water being retained just as in the ordinary bird-fountain. The neck of the retort, R, or other vessel for producing the gas, is introduced completely within the cylinder, and the water is displaced by the gas which rises and accumulates in the upper part, whilst the water runs off into a vessel placed below. The progress of the experiment may be watched by means of the glass tube, *d*, which is open both at top and bottom into the cylinder, B; the level of the water within the instrument is thus always exhibited. In order to use the gas stored up, the plug is replaced at *c*, and the stop-cock in the long pipe opened to allow the column of water to exert its pressure on the gas, which escapes on cautiously turning the stop-cock, *e*, and may either be received in a jar placed in the tray over the short tube, *e*, or it may be conveyed away through a flexible tube attached to the stop-cock, *g*.

FIG. 21.



(40) Water dissolves all gases; some in small quantities, and others with very great avidity; the latter of course cannot be collected over water. Indeed, in all cases where great accuracy is requisite, some other liquid must be substituted in the trough and jars for water. Mercury is the fluid which offers fewest inconveniences, and it is usually employed for this purpose in a trough of earthenware, iron or wood, the form of which is seen in fig. 21.

(41) *Correction of Gases for Pressure.*—The foregoing mode of collecting gases over mercury leads us to consider a correction of great importance in cases where an accurate measurement of the volume of a gas is requisite. In all cases a portion of air or gas which communicates with the atmosphere either through the walls of a flexible bag or bladder, or that is confined over water or mercury, is subject to the pressure of the atmosphere, transmitted to it either through the flexible material, or through the interposed portion of liquid. If, in the pneumatic trough, the liquid within and without the jar stand at the same level, the pressure upon the included gas will be exactly that due to the atmosphere at the time; if, however, the liquid within stand higher than that in the bath, the gas will be subjected to a pressure less than that of the atmosphere at the time, by the amount necessary to support the column of liquid above the outer level of that in the bath.

Observation has shown that the pressure of the atmosphere at the same spot is liable, from different causes, to continual variation. The average pressure at the sea-level is equivalent to that due to

a column of mercury $760^{mm.}$ (or 29·92 inches) in height; but in this climate it is sometimes so much diminished as to support a column of only about $710^{mm.}$; at other times the pressure will be equivalent to nearly $780^{mm.}$ of mercury. Now the same quantity of gas will, under these different circumstances, sometimes occupy a volume considerably greater, at others considerably less, than the average.

It is necessary, therefore, in all experiments upon the density or volume of gases, to observe the height of the barometric column, as this gives the pressure to which the gas is at the same time subjected. This, however, is true only when the liquid in the bath, and that in the jar, are on the same level. In practice it is rarely possible to make them rigidly so. The liquid generally stands highest in the jar. Supposing the gas to have been collected over mercury, in order to allow for the dilatation occasioned by this inequality of level, the difference of the two levels must be accurately measured, and the measurement so obtained must be subtracted from the height of the mercurial column in the barometer at the time. A similar correction is required if the gas be standing over water, but it is smaller in amount, a column of water of 13·596 centimetres in height being equivalent to 1 centimetre of mercury. When the necessary measurements have been made, a simple calculation shows the volume that any gas would have occupied, assuming it to have been measured under a barometric pressure of 760 millimetres.*

Suppose that having measured 50 cubic centimetres of oxygen standing over mercury, the level of the metal in the jar being $25^{mm.}$ higher than that in the bath, the barometer at the time standing at $740^{mm.}$, it is desired to ascertain what volume the gas would occupy under a pressure of $760^{mm.}$ By

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* In this country the standard or normal pressure to which gases are corrected, has been generally that of a column of mercury 30 inches in height; the French standard being that of a column of mercury 760 millimetres (or 29·922 English inches) in height: consequently 100 cubic inches, measured under the English standard pressure of 30 inches, would, under the French standard, fill a space of 100·263 cubic inches.

Strictly speaking, however, the observations should be reduced to the pressure of a column of mercury 29·922 inches in height at 32° F. Such a column, owing to the expansion of mercury by heat, would be increased $\frac{1}{5\,5\,4}$ of its length, at the mean temperature of 60° F., and consequently would then measure 30·006 inches: and under this pressure 100 cubic inches of any gas, measured at a barometric pressure of 30 inches, would be reduced to 99·98 cubic inches, a difference so trifling that it may almost always be neglected.

Boyle's law (27) the volume of a gas is inversely as the pressure. Therefore—

Standard pressure.		Observed pressure.		Observed vol.		Corrected vol.
$760^{mm.}$	:	$\left\{\begin{matrix}715^{mm.}\text{ or} \\ 749-25\end{matrix}\right\}$	::	$50^{c.c.}$	:	$\left\{\begin{matrix}x\ (=47{\cdot}039 \\ \text{cub. centim.})\end{matrix}\right.$

Or, putting the whole into a general form:—

If V be the corrected volume of the gas, V' the observed volume, H the standard height of the barometer, H' the observed height at the time of the experiment, h the difference of level in the mercurial bath; then

$$V=\frac{V'\,(H'-h)}{H}.$$

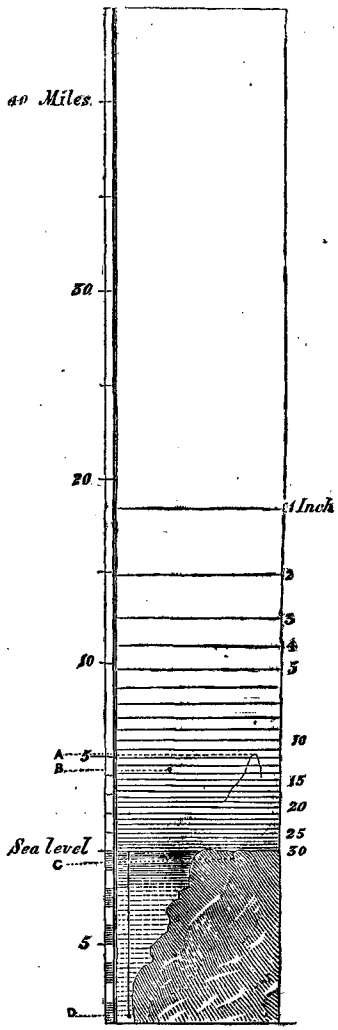
In estimating the density from the volume of a gas, it is necessary to make a further correction for the temperature (144), as well as for the state of moisture or dryness which it may possess at the time.

(42) *Density of the Atmosphere at Different Heights.*—A remarkable consequence of the law of elasticity in gases is exhibited in the increasing rarefaction of the atmosphere in ascending from the surface of the earth. The air is subject to a pressure which decreases gradually with the progressive elevation above the sea-level. This will be evident if we consider the atmosphere to be composed of a series of layers or strata: the lowest layer supports the pressure of the entire superincumbent mass; the one next above this supports the pressure of all but the lowest; the third that of all but the two lower ones, and so on in succession. In consequence of Boyle's law—viz., that the volume of a gas is inversely as the pressure, it is found that if the air be examined at a series of heights, increasing according to the terms of an arithmetical progression, the density of the air decreases according to the terms of a geometrical progression. In the following table the heights above the surface are taken in arithmetical progression, increasing regularly by distances of 3·5 miles; the *volume* of equal weights of air at these successive heights *increases* in geometrical progression, the volume being doubled for each step in the ascent; while the *density*, and the corresponding height of the barometer, *decrease* in the same geometric ratio, being at each successive elevation exactly half what they were at the preceding one:—

Density of the Air at increasing Altitudes.

Miles above the Sea.	Bulk of equal weight of Air.	Density.	Height of Barometer. Inches.	mm.
0	1	1	30·00	760
3·5	2	$\frac{1}{2}$	15·00	380
7·0	4	$\frac{1}{4}$	7·50	190
10·5	8	$\frac{1}{8}$	3·75	95
14·0	16	$\frac{1}{16}$	1·87	47·5
17·5	32	$\frac{1}{32}$	0·93	23·7

FIG. 22.



The annexed diagram (fig. 22), slightly altered from one in Tomlinson's Treatise on Pneumatics, is supposed to represent a vertical section of the atmosphere; the left-hand column shows the height in miles above or below the sea-level; the right-hand column the corresponding heights of the barometer in inches; A indicates the altitude of the highest peaks of the Himalaya; B, the altitude of 7016 metres, or 23,019 feet, the height attained in a balloon by Gay-Lussac (17 Sept., 1804);* C, Dolcoath mine, Cornwall, 260 fathoms, or 475·48 metres; D, the deepest sea sounding yet obtained, 7706 fathoms, or 8·919 miles, (Capt. Denham) H.M. ship Herald, Oct. 20, 1852, lat. 36° 49′ S., long. 37° 6′ W.†

* The height reached by Mr. Glaisher and Mr. Coxwell in their celebrated balloon ascent on Sept. 5, 1862, was about 37,000 feet (11,277 metres), or 7·137 miles.

† This very deep sounding, however, according to subsequent careful observations by American navigators, appears to be greatly in excess of the truth: the line was probably dragged by strong currents so as to have deceived the observer. The deepest soundings which appear to be worthy of confidence were obtained to the southward of the great banks of Newfoundland, and do not exceed 4·825 miles, or about 7620 metres (25,000 feet). The deepest sounding taken in the dredging expedition of 1869 was 14,610 feet, or 2·767 miles (4453 metres), on July 22, in lat 47° 38′ N., long. 12° 8′ W. The deepest

It is obvious that a knowledge of the law of the decrease of density in the atmosphere furnishes the means of ascertaining the height of mountains by the employment of the barometer.

Young has calculated that if the air continued to diminish indefinitely in density, according to Boyle's law, 1 cubic inch (16·38 cub. centim.) of air of the mean density of that at the surface of the earth would, at a distance of 4000 miles from the earth's surface (or at a distance equal to the earth's radius), fill a sphere the diameter of which is equal to that of the orbit of Saturn; and, on the other hand, if a mine could be dug 46 miles deep into the earth, the air at the bottom would be as dense as quicksilver.

The observations of astronomers upon the amount of refraction experienced by the light of the heavenly bodies in traversing the atmosphere, however, led Wollaston to consider it to be probable that there is a limit to the upper surface of our atmosphere, as definite as that of the waters of the ocean, the repulsion of the particles being at length exactly balanced by their gravitation towards the earth.

§ II. Cohesion.

(43) In the case of gases the predominance of elasticity due to repulsion is the leading characteristic; in the case of solids the opposite property of cohesion is that which first demands attention. Cohesion is the action which binds together the same kind of particles into one mass. It is this action which retains a bar of iron, a block of wood, or a lump of ice in a single piece.

It is obvious that the cohesion of different bodies varies greatly. Cohesion, however, appears to be uniform between particles of the same kind placed under circumstances similar as to temperature and structure. Owing to the difficulty of securing uniformity in texture and freedom from flaws, even in the most compact substances, such as the metals, it is difficult to estimate the coefficient of cohesion in any material with precision; although the general fact that iron is much tougher than copper, and copper than lead, is at once recognised. Two methods have been generally used to determine the cohesion of solids; the first consists in estimating the tension required to stretch rods of a given diameter of the substance under examination, until they give way; the second, in finding the amount of pressure required to crush a cube of the substance of given dimensions.

The strength of materials, all-important as it is to the engineer and to the architect, has little to do with chemistry, although variations in cohesion and aggregation of the same substance exercise a marked influence on the rapidity of many chemical actions. Gunpowder, for example, is reduced to grains in order that each portion may ignite quickly, and contribute its pressure to act upon the bullet; but the very same material, before it has been

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sounding yet obtained was during the expedition of the Challenger, on March 23, 1875, in lat. 11° 24′ N., long. 143° 16′ E., where the depth was 4575 fathoms, 27,540 feet (8366 metres), or 5·199 miles.

granulated, and whilst in the form of hard compact masses, as it comes from the press, burns comparatively slowly, like a fuse, or a portfire.

(44) *Reunion of Divided Solids by Cohesion.*—Particles of a similar nature will, under the influence of cohesion, reunite, after complete separation, if brought sufficiently near to each other. This is shown on pressing together two clean, smooth, and freshly-cut surfaces of lead; they will cohere, and a tension of some pounds will be required to separate them. In the same way, too, perfectly polished plates of glass cohere, sometimes so completely that they may be cut and worked as a single piece. This has happened in plate-glass manufactories.

This cohesion of divided solids is well exemplified by Whitworth's planes. These consist of two masses of cast iron with true surfaces, which when pressed together require the exertion of considerable force to separate them, so that the lower mass may be raised by lifting the upper one. Tyndall has shown that this phenomenon is observed in vacuo as well as in air.

According to the ratio that cohesion bears to other actions which, like heat and elasticity, tend to separate the particles of matter from each other, the body assumes the solid, the liquid, or the aëriform state. Considerable differences in physical properties are produced both in solids and in liquids by variations in the degree of cohesion existing among their particles.

(45) *Cohesion of Solids.*—In solids, these variations give rise to differences in hardness, elasticity, brittleness, malleability, and ductility.

The *hardness* of a body is measured by its power of scratching other substances, and it consists in the degree of resistance which the particles offer to the slightest change of relative position. To the mineralogist, the variations in the degree of hardness presented by different crystallized bodies, often furnish a valuable physical sign by which one mineral may be discriminated from others which resemble it. For the purpose of facilitating such comparisons, Mohs selected ten well-known minerals, which are enumerated in the following table, each succeeding one being harder than the one which precedes it: thus arranged, they constitute what he terms a *Scale of Hardness*, which has been generally adopted. In the examples selected, each mineral is scratched by the one that follows it, and the hardness of any mineral may be determined by reference to the types thus chosen. Suppose, for example, a body neither to scratch nor to be scratched by fluor spar—its hardness is said to be 4: if it should scratch fluor spar, but not apatite, its

hardness is between 4 and 5; the degrees of hardness being numbered from 1 to 10. The figures on the right indicate the number of minerals known of the same, or approximatively the same degree of hardness, as the substance opposite to which they stand:—

Scale of Hardness of Minerals.

1	Talc	23	6 Felspar (any cleavable variety) . 26
2	Compact gypsum, or rock salt .	90	7 Limpid quartz 26
3	Calc spar (any cleavable variety)	71	8 Topaz 5
4	Fluor spar	53	9 Sapphire, or corundum . . . 1
5	Apatite (crystallized)	43	10 Diamond 1

The cause of the varieties of hardness observed in different bodies is not well understood. Even in the same substance, trifling variations in the external circumstances to which the body is subjected often produce extraordinary differences in the degree of hardness which it exhibits. A piece of steel cooled slowly from a red heat is comparatively soft; it may be cut with a file; and under strong pressure, it will even take impressions from a die: whilst the same piece of steel, if heated to redness, and suddenly cooled, becomes as brittle as glass, and nearly as hard as the diamond.

Brittleness is exhibited by bodies the particles of which resist displacement with regard to each other, except within extremely narrow limits. It is generally observed in hard and elastic substances.

Malleability and *ductility*, or the property of extending under the hammer, and of fitness for drawing into wire, are the opposite of brittleness, the molecules of the solid admitting of very considerable relative displacement without losing their cohesion. These modifications of cohesion are exhibited only by the metals, and by a few only of them.

(45 *a*) *Viscosity of Fluids.*—Amongst liquids, considerable differences are observed in the degree in which the cohesion is exhibited. *Limpid* liquids are those which, like ether or spirit of wine, display great mobility of their particles; bubbles produced in such liquids by agitation, rise quickly to the surface, break and disappear. In oil, syrup, and gum-water, the particles move sluggishly; such liquids are termed *viscous*. The viscosity of liquids presents a certain analogy with the malleability of solids. In a few instances, whilst the solid is melting under the influence of heat, a viscous state is observed intermediate between the hardness of solids and the perfect mobility of liquids. Melted sugar, or barley-sugar, is a case in point. The occur-

rence of viscosity, as an intermediate state, is rare, except in the case of a mixture of two substances, one of which melts at a temperature a little higher than the other. Glass, which is a mixture of several silicates of different degrees of fusibility, offers a striking example of this kind; indeed to this condition it owes the plastic properties by which it is rendered capable of adaptation to the multifarious purposes to which it is now applied. Other bodies, such as the different varieties of wax and fat, soften, without being actually viscous, before they finally melt. A true chemical compound usually passes at once from the solid to the liquid form, as when ice, for example, by fusion, becomes water. A few of the simple bodies, however, present some remarkable cases of the occurrence of viscosity preceding fusion; such, for instance, as phosphorus, and those metals which, like iron and potassium, admit of being 'welded,' a process in which two pieces of the metal are united into one mass by hammering or pressing them together whilst they are in the soft condition which is observed before fusion.

(46) *Influence of Heat on Cohesion.*—All analogy leads to the conclusion that cohesion would be entirely destroyed in every elementary body by a sufficient elevation of its temperature; though there are some bodies which have not as yet been liquefied, and many which have not been converted into vapour. The three conditions in which the same chemical compound may exist, exemplified by ice, water, and steam, according to the temperature to which it is exposed, are shown by a vast number of other bodies. Gold itself has been first melted and then volatilized by the intense heat of the sun's rays, concentrated by a burning lens. On the other hand, by a sufficient reduction of temperature, united with a certain degree of pressure, a number of gases have been reduced, first to the liquid, and several even to the solid condition. The action of cohesion, like that of heat, is therefore universal. If the repulsion exerted by heat could be carried sufficiently far, there is reason to believe, that every known substance, not actually decomposable by heat, might be made to appear as a gas; and, by a reduction of temperature sufficient to allow cohesion to exert its sway, every known gaseous substance would probably exist in the solid state.

In gases, cohesion appears to be entirely overcome, and it does not exert itself sensibly, except in cases where the gas is approaching the point at which, by increase of pressure, or reduction of temperature, it assumes the liquid form (*Note*, § 27 and 197).

§ III. Adhesion—diffusion of liquids and gases.

(47) *Adhesion.*—Analogous to cohesion, or the action which holds similar particles together, is that of adhesion, which is exerted between the particles of dissimilar kinds of matter. It not unfrequently rises high enough to destroy cohesion, as when sugar or salt becomes dissolved in water. A rod of glass or of wood dipped into water or oil comes out wetted in consequence of this action. It is exerted between different bodies with very different degrees of intensity, as may be illustrated by the following experiment:—

Take two glass dishes, sift over the bottom of one a layer of lycopodium or of finely-powdered resin, and over the other a layer of powdered glass: if a little water be sprinkled upon each, the drops of water in the dish of resin will be covered by a thin film of the powder, and when the dish is inclined will roll about like shot, the cohesion of the particles of the liquid predominating over their adhesion to those of the solid: whilst on the powdered glass, from the superior adhesion of glass to water, the drops sink in and are absorbed.

If the solid becomes wetted, a certain preponderance of the adhesion over the cohesion of the particles is obviously necessary; for if the cohesion exceeds the adhesion, as when glass or iron is plunged into mercury, the solid is not wetted. Extraneous circumstances, however, greatly modify the exertion of this action. If a film of air, of oil, or of any foreign matter, be diffused over the surface of the solid, it is no longer the surface of the solid and the liquid which are concerned, but the liquid and the surface of air or of oil with which the solid is covered. A clean glass is immediately wetted with water, but if the slightest film of grease exist upon its surface, the water runs off almost entirely.

Adhesion gives rise to a variety of important phenomena; it is mainly concerned in the production of capillary action, of solution, and of the diffusion of liquids; it is also exerted in osmosis, and less directly in the process of the intermixture and diffusion of gases. In this chapter some remarks will therefore be made upon each of these subjects in succession. Adhesion is the more especially worthy of attentive study by the chemist, because in its manifestations it is more nearly allied than any other force to chemical attraction.

Adhesion is exerted between bodies of all kinds, and when it occurs between solids, it is the principal cause of that resistance to motion which is termed *friction*. As a general rule, friction is greater between similar kinds of matter, less between those which differ in nature. An iron axle moving in an iron socket expe-

riences under similar circumstances a greater amount of friction than if revolving in a brass socket; and the interposition of a substance like plumbago or grease, the particles of which have but very little cohesion, is a familar mode of reducing the amount of friction in machinery.

Few substances admit of a greater variety of useful applications from their faculty of adhesion than caoutchouc; its perfect adhesion to glass adapts it admirably for stoppers, and enables the chemist to employ it for air-tight and flexible joints. This property of adhesion to the bodies which it touches further fits it for bands for driving machinery, and for numberless other purposes.

(48) *Cements.*—The entire value of cements depends upon the operation of adhesion; and in the variety of cements rendered necessary by the variety of materials to be united, we have additional proof that adhesion is exerted between different kinds of matter with very varying degrees of intensity. Glue or gum may be used for joining pieces of pasteboard or wood, while it totally fails as a cement for glass or china, either of which needs some resinous material to unite its fragments; whilst for the union of marble, stone, or brickwork with each other, the use of mortar or some calcareous cement is required. The thinner the layer of cement, the more perfectly does it perform its task, as it more rapidly and completely adapts itself to changes of temperature, which, by causing it to expand unequally, would destroy the cohesion of its own particles if a thick mass were employed.

Cements of various kinds are in continual requisition in the laboratory. Well-boiled paste applied on thin paper forms an excellent covering for corks and other joints which are liable to be porous; it must be allowed to become nearly dry before it is used. Plaster of Paris made into a paste, not too stiff, may often be used; when dry it may be washed over with oil or melted paraffin to make it air-tight. Strips of well-soaked bladder may sometimes be employed advantageously; they form a firm joint when dry: but for most purposes where a temporary joint only is required, nothing is so convenient as a strip of sheet caoutchouc softened at the fire, and bound round the parts to be connected; when softened thus, it usually adheres perfectly without even requiring to be tied. When the joint is intended to be permanent, as, for example, when a brass cap is to be attached to the neck of an air-jar, a resinous cement, consisting of 5 parts of resin, 1 of yellow wax, and 1 of finely-powdered Venetian red, forms a convenient mixture: the resin and wax are melted together and incorporated with the Venetian red by stirring. Before applying it, both the glass and the metallic cap which are to be connected together must be warmed just sufficiently to melt the cement. When the joints are required to resist a considerable pressure without leaking, a mixture of equal parts of red and white lead ground into a paste with linseed oil, worked up with fibres of tow, and packed tightly into the joint, sets firmly, and is not liable to crack.

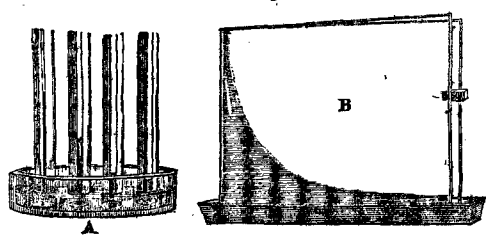
It not unfrequently happens that the adhesion between a cement and the bodies which it unites, surpasses the cohesion of the particles which compose the bodies themselves; from this cause we often see a film of wood split off, adhering to the surface of the glue, when a fracture occurs near one of these

joinings. The feat of splitting a bank-note into two laminæ, which excited so much astonishment, was accomplished by cementing it firmly between two flat surfaces, and afterwards separating them; the cohesion of the paper being feebler than the adhesion to the cement, the paper was split through the middle. This method of splitting paper had, however, been long known to the buhl-cutter and inlayer.

(49) *Capillarity.*—The existence of adhesion between solids and liquids is so well known as to need no further illustration; but it produces many very important results, some of which must be noticed.

It is to the adjustment of adhesion and cohesion between solids and liquids under the simultaneous influence of gravity, that the important phenomena of *capillarity* are due. If a perfectly clean glass tube, with a fine bore, and open at both ends, be plunged into water, or into any liquid capable of wetting it, the liquid will be found to rise in the tube considerably above the level of the surface in the vessel; and the finer the tube the higher does the liquid rise. The surface of the liquid will also be seen where it approaches the outside of the tube, or the side of the vessel containing it, to stand above the general level (fig. 23, A). The phenomenon may also be examined by placing vertically in a shallow vessel containing a little coloured liquid, two plates of glass with parallel faces, which are in contact by two of their vertical edges, and slightly separated at the opposite edges. The liquid will rise between the glass plates, the height of the column being inversely as its distance from the angle of contact between the plates. The upper boundary of the liquid will consequently describe a hyperbolic curve (fig. 23, B). The cause of the rise of the liquid is the adhesion between its particles and those of the glass; the limits to that rise are the action of gravity, and the cohesion amongst the liquid particles. As the action of gravity is equal under ordinary circumstances upon all the particles of the liquid, it reduces the liquid surface to a uniform level. When a tube is introduced, the uniformity of this action is interfered with, as the following considerations will show:—the particles in immediate contact with the side of the tube are partially supported by adhesion to its surface;

FIG. 23.



a longer column therefore becomes necessary in order to compensate for the diminution of downward pressure. Now let us conceive the particles of the elevated column of liquid to be arranged as a series of contiguous concentric cylinders: the particles of the outermost cylinder are sustained laterally by adhesion to the tube, those of the next cylinder are hung on to these, if the expression may be allowed, and supported solely by cohesion with their fellows; those of the third cylinder are hung on to the particles of the second, and so on, till we reach the central rod of particles. The surface of the liquid is in consequence necessarily curved;—the outer cylinder, or the portion of liquid in contact with the tube standing at the highest point. Now since adhesion is confined to the superficial layer, and, between the same substances, is *cæteris paribus*, constant in quantity for an equal extent of surface, the wider the tube the shorter will be the column sustained, as the contents of the column raised by cohesion increase more rapidly than the surface of the cylinder. The height of the column is found to be inversely as the diameter of the tube.

(50) *Variations in Capillarity.*—The elevation of the column of liquid in tubes of equal diameter varies with the nature of the liquid, the variation depending partly on the difference of cohesion between the particles of the liquid, partly upon the difference of adhesion between the liquid and the glass. In consequence of the decrease of both these forces by heat, the height of the column diminishes as the temperature rises.

The following table from the experiments of Frankenheim shows the height at which the different liquids enumerated stand, at 0° C. in a tube 1 millimetre in radius, (about $\frac{1}{25}$ of an inch,) with the coefficient of correction for temperature, which multiplied by t, the number of degrees centigrade above 0° C., gives the amount to be deducted in millimetres from the number in column 3, in order to find the height of the capillary column at the temperature required:—

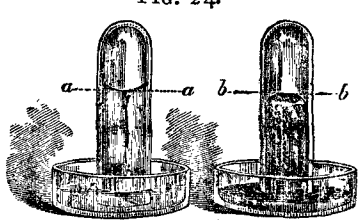
Capillary Elevation of Liquids in Glass Tube of 1 *mm. Radius, at* 0° *C.*

Liquid used.	Density at 0° C.	Height in millimetres of the capillary column.	Height of the column in thousandths of an inch.	Coefficient for correction for Temperature.
Water	1·0000	15·336	604	$-\ 0{\cdot}02875t$
Acetic Acid	1·0522	8·510	335	$-\ 0{\cdot}0097t$
Sulphuric Acid ...	1·8400	8·400	331	$-\ 0{\cdot}0153t + 0{\cdot}000094t^2$
Oil of Lemons... ...	0·8380	7·23	285	$-\ 0{\cdot}0174t$
Oil of Turpentin ...	0·8902	6·76	266	$-\ 0{\cdot}0167t$
Alcohol (dilute) ...	0·9274	6·41	252	$-\ 0{\cdot}0120t$
Alcohol	0·8208	6·05	238	$-\ 0{\cdot}0116t + 0{\cdot}000051t^2$
Ether	0·7370	5·40	213	$-\ 0{\cdot}0254t$
Carbonic Disulphide	1·2900	5·10	201	$-\ 0{\cdot}0101t$

(51) *Capillary Depression of Mercury.*—In liquids, such as mercury, where the cohesion preponderates over their tendency to adhere to the sides of the tube, the capillary action is reversed; the surface becomes convex instead of concave, and the height of the column within the tube is depressed below the general level. In a mass of liquid, each particle is maintained in its place by the mutual attraction of all the surrounding ones; but if a column be isolated from the mass of liquid by the interposition of the walls of the tube, the sides of which exert little or no equivalent adhesion, the cohesion of the mass below draws down the upper particles, and produces a depression of the column. This depression of mercury in glass renders a certain correction necessary in reading off the height of the mercurial column in the barometer, which always stands a little lower than the elevation due to the atmospheric pressure. The narrower the bore of the tube the greater is the depression. Experiment has shown that this capillary depression is nearly one-half less in tubes that have had the mercury boiled within them, than in unboiled tubes, as the process of boiling expels the film of air, which adheres to the glass in unboiled tubes. By employing a tube of 16 or 20 millimetres in the bore, this correction becomes so trifling that it may be neglected. In a tube of $6^{mm.}$ ($\frac{1}{4}$ inch) in diameter in which the mercury has been boiled, the depression is $1{\cdot}171^{mm.}$, while with a similar tube of $13^{mm.}$ in diameter it is only $0{\cdot}223^{mm.}$ The capillary depression of mercury is slightly increased by elevation of temperature.

In reading off the level of mercury in a barometer, or in a graduated jar used for the measurement of gases, the height of the metal should be taken from the convexity of the curve; but in estimating the volume of a liquid which wets the surface of the glass the determination should always be made from the bottom of the curve. The lines *a a*, *b b*, fig. 24, indicate the points in the two cases.*

FIG. 24.



(52) *Importance of Capillary Actions.*—Capillarity plays an important part in the operations of nature, and in a variety of ways has been rendered subservient to the wants of man. A

* In accurate observations on the volume of gases confined over mercury, it becomes necessary to estimate the amount of error which is thus introduced.

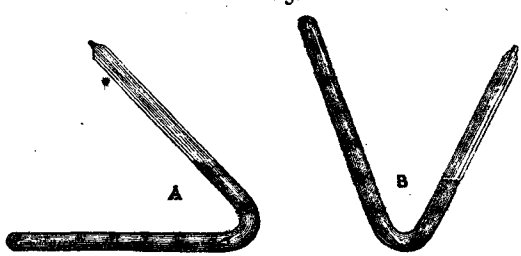
familiar illustration of its employment is seen in the wicks of lamps and candles, which, being composed of a bundle of fibrous materials, furnish hair-like channels by which the oil or melted combustible is elevated to the flame, and supplied as fast as it is consumed. Capillarity influences the circulation of the liquids in the porous tissues of organized beings, and it is the principal mode in which water, with the various substances which it holds in solution, is supplied to the roots of growing plants. By its means, during the droughts of summer, fresh supplies of moisture are raised towards the surface, for the maintenance of vegetable life; and in the same way, when during winter the surface is hard bound by a long dry frost, water is constantly finding its way from beneath, is solidified upon the surface, and remains stored up until a thaw ensues; when this occurs, the accumulated moisture mellows the soil and produces the well-known soft and plashy state of the ground which follows long-continued frosts, and which extends deeper, the longer the duration of the freezing temperature, although neither snow nor rain may have fallen. Few persons are aware of the immense action which may be developed by capillarity; if a plug of dried wood be fitted into a strong glass tube, and the end of the plug be immersed in water, the wood becomes swelled by the imbibition of liquid owing to capillary action, and the tube is split. In some parts of Germany this action is turned to account in splitting millstones from the rock: holes are bored into its substance in the direction in which it is to be split, and into these holes wedges of dry wood are driven tightly; when exposed to moisture they swell, and large blocks of stone are thus detached with little labour or expense.

A curious illustration of the combined action of cohesion and adhesion, in overcoming gravity, is afforded by the following experiment:—Procure a small cylinder of fine copper-wire gauze, about 8 centimetres or 3 inches high, and 5 centimetres wide, closed also above and below with the same material, and furnished with a stout wire to serve as a handle; plunge it under water; considerable difficulty will be experienced in expelling the air, owing to the formation of a film of moisture over its surface, which, by the cohesion of the liquid particles composing it and by its adhesion to the wire gauze, prevents the escape of the air; when about half filled with water, lift the cylinder out of the liquid—the liquid will be securely retained: water may even be allowed to fall in a gentle stream upon the top of the gauze, when it will pass through and run out below, without, however, affecting the quantity of liquid within; but by giving the handle a slight jerk, the film of liquid which supported the pressure of the atmosphere will be broken, and the water will then immediately escape. (For a more complete treatise on Capillarity, the student is referred to Professor Clerk Maxwell's *Theory of Heat*, and to the article, *Capillary Action*, by the same author, in the ninth edition of the *Encyclopædia Britannica*, 1876.)

(53) *Cohesion of Liquids.*—In liquids, notwithstanding the facility with which their particles slide one over the other, and the unlimited freedom of motion of each molecule within the mass of liquid, a very appreciable amount of cohesion still exists, and is displayed in the rounded form assumed by every detached drop. This same form of cohesion is also beautifully shown in the case of two liquids which do not dissolve each other, but which have precisely the same density, as is the case with oil and spirit of wine of a certain degree of dilution: if a little oil be poured into such diluted spirit, it remains suspended within it in the form of a perfectly spherical mass. In the drops of dew which fringe every leaf in a fine summer morning, we have an admirable natural illustration of this fact. A striking exemplification of cohesion in the particles of liquids is also afforded by blowing a large soap-bubble upon the end of a glass tube: upon presenting the open end of the tube to a lighted taper, whilst the bubble is still attached to the other end, the contraction of the film expels the air with sufficient velocity to extinguish the taper.

The researches of Donny (*Ann. Chim. Phys.* 1846 [3], xvi. 167) have added many curious facts to our knowledge of the cohesion of liquids. The following form of one of his experiments may be cited as an illustration:—A tube, A, fig. 25, about 1 metre or 40 inches long, and $25^{mm.}$ or 1 inch in diameter, is bent at its middle to an angle of about 60°; it is sealed at one end, and filled with distilled water, which, when the tube is closed, is to occupy about two-thirds of its capacity; the water is thoroughly boiled for an hour, and the tube is then hermetically closed while boiling. In this condition the tube contains only water and the vapour of water. After it has been carefully reversed, as at A, it may be brought into the position represented at B, and the water will nevertheless be supported above the level of the liquid in the other limb by adhesion to the surface of the glass, and by the cohesion among its own particles. If now the tube be inclined in such a manner that a minute bubble of aqueous vapour is made to pass up into the full limb, the column of water, having its continuity broken, at one point, immediately falls, and the level of the liquid in both limbs becomes the same.

FIG. 25.



The same phenomenon is often observed in the filling of barometer tubes. In order to remove the air completely, the mercury is boiled in the tube (52), and it not unfrequently happens that, when the tube is inverted after cooling, the mercury adheres so strongly to the glass that the column does not fall to the usual barometric height. A concussion separates the mercury from the glass,

but on inclining the tube so as to allow the liquid to rise to the top, the adhesion is not again manifested.

(54) *Influence of Surface on Adhesion.*—Since adhesion takes place solely between the surface of bodies, it is evident that any circumstance which increases the extent of that surface must materially facilitate the exertion of this force. Minute subdivision, by thus increasing the extent of surface, greatly exalts the effect of adhesion:—for example, a cube of 1 centimetre in the side exposes a surface of 6 square centimetres; *i.e.*, there is a square centimetre upon each of its 6 faces; if this cube be subdivided into a number of smaller cubes, each of which is only $\frac{1}{100}$ of a centimetre in the side, it would furnish 1,000,000 of these minute cubes. Now as each little cube has 6 sides, the surface which it will expose is $\frac{6}{10000}$ of a square centimetre, or 10,000 of them will expose 6 square centimetres; that is, as much surface as a solid cube of a centimetre in the side: the 1,000,000 cubes will consequently expose 100 times as great a surface, or 600 square centimetres. The adhesion, therefore, by such a subdivision, should be increased somewhat in this proportion.

The influence of this kind of subdivision in exalting the effect of adhesion is strikingly exhibited in the case of charcoal. The structure of the wood from which the charcoal is procured is cellular: when heated in vessels from which air is excluded, the volatile constituents of the wood are expelled; and the charcoal, which does not fuse, remains behind in a very porous condition, retaining the form of the wood which furnished it. Mitscherlich has calculated that the cells of which a cubic inch of boxwood is formed expose a surface of not less than 73 square feet.

Adhesion occurs between charcoal and other bodies in very different degrees. For many colouring matters of vegetable and animal origin this adhesion is extremely energetic; so that if these bodies be dissolved in any liquid and agitated with charcoal, nearly the whole of the colouring matter will be retained by the charcoal, and on separating the latter by filtration, the liquor will run through colourless. Ordinary vinegar and port-wine may thus be obtained in a colourless condition. Advantage is taken of this fact in the refining of sugar, in which process the syrups are deprived of colour by filtration through a column of charcoal 30 or 40 feet (12 metres or more) in thickness. The species of charcoal which is most extensively employed for this purpose is that obtained by burning bones in closed vessels; and it is hence termed *bone black*, or *ivory black*, or frequently *animal charcoal*. The charcoal is in this case in a state of extreme sub-

division; it does not constitute above a tenth or a twelfth of the weight of the mass; the remainder consists of earthy matters; chiefly calcic phosphate and carbonate. When bone black has been used for filtering liquids, and has ceased to take up any more colouring matter, it is thrown aside and allowed to ferment: if then it be well washed, and re-burned, it may be used again with nearly equal effect. Other animal matters, especially dried blood, furnish, when calcined and well washed, a charcoal which is still more efficacious. The addition of potassic carbonate to the mass before calcination, still further increases the decolorizing power.

Many other matters besides those possessed of colouring properties have likewise this peculiarity of adhering strongly to charcoal. Graham has shown that metallic oxides in solution in potash or ammonia, arsenious acid in water, and bodies generally of feeble solubility, possess this property; a variety of vegetable matters, and especially the bitter principles, are thus affected. If porter be agitated with charcoal and filtered, it will not only be deprived of colour, but also of much of its bitterness. It was formerly the practice, after the active principles of medicinal plants had been separated from the woody fibre and most of the extraneous matters with which they are associated, to free them from the colouring matters with which they were contaminated, by digestion with animal charcoal; so large a proportion of the active principles themselves, however, was found to be retained by the charcoal, that the plan was abandoned. In consequence of this property, animal charcoal has been administered with good effect in some instances of poisoning with vegetable matters: in such cases it can never be unsafe, and may often be of great value. I have found that very dilute aqueous solutions of salts of lead are decomposed by filtration through a column of animal charcoal: plumbic nitrate, acetate, and chloride, each part with their metallic base, which is retained by the charcoal, probably as a basic salt; whilst free nitric, acetic, or hydrochloric acid is found in the filtered liquid.

Many finely-divided substances besides charcoal, such as hydrated ferric oxide, hydrated alumina, hydrated antimonious sulphide, hydrated bone phosphate (tricalcic diphosphate, $Ca_3P_2O_8$), as well as plumbic iodide and sulphide when freshly precipitated, also exert powerful decolorizing actions. The decolorizing power varies for each substance with the nature of the colouring principle: thus tincture of litmus yields its colouring matter more readily to calcic phosphate, and to hydrated ferric oxide, than it

does to animal charcoal freed from bone phosphate by the action of acids. On the other hand, the colouring matter of red wine and of molasses is more readily absorbed by animal charcoal than it is by hydrated calcic phosphate, or ferric oxide. (Filhol, *Ann. Chim. Phys.*, 1852 [3], xxxv. 206.)

(55) *Solution.*—Adhesion is frequently manifested between solids and liquids sufficiently to overcome cohesion, and the substance is then said to become dissolved, or to undergo solution. In this manner sugar or salt is dissolved by water, camphor or rosin by spirit of wine, lead or silver by mercury. Anything that weakens cohesion in the solid favours solution. For instance, if the substance be powdered, it becomes dissolved more quickly, both from the larger extent of surface which it exposes, and from the partial destruction of cohesion. In the same way, heat, by increasing the distance between the particles of the solid, lessens its cohesion, and probably thus contributes so powerfully to assist in producing solution. If a solid body be introduced in successive portions into a quantity of a liquid capable of dissolving it, the first portions disappear rapidly, and as each succeeding quantity is added, it is dissolved more slowly, until at length a point is reached at which it is no longer dissolved. When this occurs, the cohesion balances adhesion, and the liquid is said to be *saturated.* It is important to remark, that in cases of simple solution, the properties both of the solid and of the liquid are retained. Syrup, for instance, retains the sweetness of the sugar and the liquid form of water. So, when camphor is dissolved in spirit of wine, the resulting tincture partakes of the properties of both, having the smell and taste both of camphor and of spirit. Solution is, in this respect, distinguished broadly from those cases in which a solid disappears under the influence of a liquid owing to the exertion of a chemical force between the particles of the two bodies; as when copper is dissolved by nitric acid, or iron by sulphuric acid. Solution usually occurs more readily when the solvent and the body dissolved present some general resemblance in properties: for example, mercury dissolves many of the metals, alcohol dissolves resins, oils dissolve fatty bodies and each other. Mere solution is attended by depression of temperature, but where the formation of a hydrate (or definite chemical compound with water) occurs, elevation of temperature is produced, a circumstance which, as Graham remarks, indicates an essential difference between solution and chemical combination. It is, however, possible that in cases which appear to be merely those of solution a chemical action

takes place, but that the heat developed is more than counterbalanced by the quantity absorbed in the conversion of the solid into a liquid. The solution of sodic sulphate in concentrated hydrochloric acid produces intense cold; but it seems probable that the rapid conversion of the solid into a liquid is due to chemical action. Again, the freezing mixtures obtained by mixture of ice with sodic and calcic chlorides would appear to owe their efficacy to the chemical attraction existing between these salts and water, but which cannot take place until the ice is liquefied. The view that solutions are combinations of the dissolved bodies with the solvents, is also supported by the changes which occur in some solutions by the action of heat; thus the diminution of solubility of some salts by heat appears to be due to the existence at the higher temperature of a hydrate containing less water, and the changes of colour of solutions of cobalt salts when heated, may be ascribed to the same cause. In cases of chemical action, on the other hand, that action is most energetic between bodies the properties of which are most widely different; the metals, for example, are dissolved by acids, oils by the alkalies, and silica, if melted with potash or soda, becomes soluble in water. The extent to which different solids are dissolved by the same liquid varies almost indefinitely. In water, baric sulphate is almost absolutely insoluble; calcic sulphate or gypsum is soluble in the proportion of about 1 part in 700 of water; potassic sulphate in about 1 part in 16; while magnesic sulphate may be dissolved to the extent of 2 parts of the crystals in 3 of water. It should be observed that water, after it has been saturated with one salt, will still continue freely to dissolve others.

Many substances in which the cohesion amongst their particles is weak are extensively soluble in water, though they have but little adhesion to it. Such substances will often be displaced by adding a solution of another body which adheres more strongly to water. Prussian blue, for example, is dissolved by distilled water which has been acidulated with oxalic acid; but it is precipitated by adding a solution of common salt, or of sodic sulphate, and the blue compound subsides on standing, leaving a clear colourless liquid above it.

Although in the majority of instances the solubility of a substance is increased by heat, it is not uniformly so. Lime and several of its salts offer remarkable exceptions. Water just above the freezing point dissolves nearly twice as much lime as it does when boiling; so that if water, saturated with lime in the cold, be

heated, it becomes milky, and recovers its transparency as it cools. Calcic sulphate is also slightly more soluble in water at about 100° F. (38° C.) than it is in boiling water. A compound of lime and sugar, very soluble in cold water, is separated from the solution almost completely, if heated to boiling. But the most remarkable case of the kind occurs in sodic sulphate: this salt (the Glauber's salt of commerce) when crystallized requires about 10 times its weight of ice-cold water for solution, and its solubility increases rapidly as the temperature rises, until it reaches 33° (C. 91°·4 F.): from this point until the solution boils, the solubility decreases; so that when a portion of the liquid saturated at 33° is heated more strongly without allowing the water to evaporate, hard gritty crystals are deposited, and the liquid when it boils retains only about four-fifths of the quantity which was dissolved at 33°. Sodic seleniate exhibits the same peculiarity; so also does ferrous sulphate, although in a less degree. These anomalous results may be partly explained by the consideration, that heat diminishes the force of adhesion as well as that of cohesion; generally speaking, cohesion is the more rapidly diminished of the two, although not uniformly so; and in the cases of which we are now speaking, it would appear that the adhesion to water decreases in a greater ratio than the cohesion of the saline particles. An important observation in relation to this subject has been made upon the composition of the salts just mentioned, which have been found to undergo a change at a temperature below that of boiling water: at the temperature of the air, these salts contain a certain quantity of water, known as *water of crystallization*; but this water is either wholly or partially expelled from the crystals at a boiling heat. The hard crystals of sodic sulphate which are deposited during the heating of the saturated solution contain no water. The supersaturation of saline solutions has been made the subject of an elaborate series of researches by Löwel, as well as by Gernez, Jeannel, Tomlinson, and De Coppet. In the course of these inquiries, it appeared that in many instances a salt which ordinarily crystallizes with a large proportion of water may be obtained in two or more different crystalline forms, in each of which it is generally united with a different quantity of water of crystallization. Sodic sulphate, for example, may be obtained in three different forms—viz., 1, the anhydrous salt (Na_2SO_4); 2, a hydrate with 7 H_2O; and 3, a hydrate with 10 H_2O. Each of these varieties has its specific solubility, which differs from the solubility of the other varieties of the same salt. It is, therefore, possible to have two or more solutions of the same salt at the

same temperature, each of which shall be saturated, and yet each of which shall contain, in equal weights, different quantities of the salt, when reduced to its anhydrous condition—the variation depending upon differences in the molecular constitution of the salt. Sodic carbonate (Na_2CO_3), besides its ordinary form with 10 H_2O, crystallizes in two different forms, each of which, singular to say, contains 7 H_2O; but the solubility of these two varieties is different; and a similar observation has been made in the case of magnesic, zincic, ferrous, and cupric sulphates, and a few other salts. Salts which do not yield hydrated crystals never furnish supersaturated solutions.*

Diffusion of Liquids.

(56) *Adhesion between Liquids.*—In the majority of instances adhesion between dissimilar liquids is very perfect; and, from the complete mobility of the particles, the two liquids become perfectly incorporated. A drop of alcohol or of oil of vitriol may be perfectly mixed with a quart or any other quantity of water; or a drop of water with a quart of alcohol or of oil of vitriol. There are instances, however, in which this perfect solution does not take place: the cohesion of the particles of the two liquids may, at a certain point, balance their adhesion for each other, and they will become mutually saturated. For this reason, when ether is mixed with water by agitation, the greater part will separate on allowing the mixture to repose: the ether will have dissolved an eighth or a tenth of its bulk of water, and the water will have taken up about an equal proportion of ether. In a similar way the essential oils are soluble only to a very small extent in water; oil of peppermint, for instance, if agitated with water, and then left to rest, will, for the most part, separate, although a sufficient quantity will have been dissolved to communicate the flavour and odour of the essence to the water. In

* Gernez enumerates about 24 other salts in addition to those mentioned above, as being able to furnish supersaturated solutions. Among these he includes potash and ammonia alum, and several double sulphates, sodic and ammonic phosphates; ammonic, strontic, and uranic nitrates; sodic, zincic, and plumbic acetates: potassic arseniate, ammonic oxalate, as well as sodic borate, thiosulphate, (hyposulphite), and citrate; together with citric and tartaric acids.

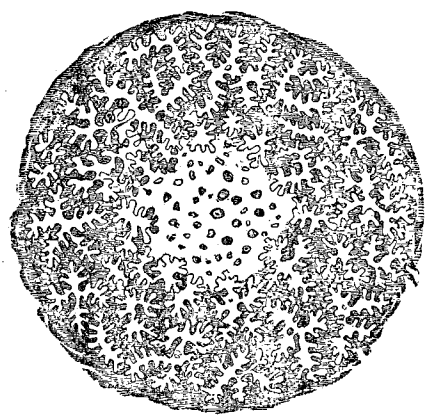
Such supersaturated solutions crystallize at once on the addition of a crystal of the salt itself, and often by contact with a glass or metallic rod, possibly owing to the action of the film of air which adheres to their surface. By a sufficient reduction of temperature, all these supersaturated solutions crystallize, some requiring a much lower temperature than others.

other instances, the separation of the two liquids, as when oil and water are mingled, appears to be complete.

When chloroform is dropped into distilled water it sinks gradually, and the drops preserve their rounded outline: but if a drop or two of an alkaline solution be added, the surface of the chloroform becomes flattened; and it resumes its rounded character on again adding a few drops of an acid. This experiment shows what slight circumstances may modify the cohesive powers of a liquid, and its degree of adhesion to others; the adhesion of water to chloroform being increased by the addition of an alkali, and being again diminished by neutralizing the alkali.

(57) *Cohesion Figures.*—A curious illustration of the struggle between the forces of cohesion and adhesion is exhibited in the phenomena of *cohesion figures*, to which attention has been drawn by Tomlinson. (*Phil. Mag.* 1861 [4], xxii. 249, and 1862 [4], xxiii. 186.) These phenomena may be best examined by allowing a drop of some liquid sparingly soluble in water, such as kreasote, or one of the essential oils, to be deposited gently upon the surface of clean water in a wide glass vessel perfectly free from grease:* the adhesion of the drop to the surface of the water will cause it to spread out into a film, but the cohesion of the particles composing the drop immediately produces a reaction; if oil of lavender be used, the film opens in a number of places, producing a worm-eaten pattern, resembling that shown in fig. 26. The arms of this figure tend to gather themselves up into separate smaller drops, the adhesion of the water spreads them out again, then the cohesion of the oil reacts against this, and soon prevails: the consequence being the speedy formation of the original drop into a number of discs, with sharp, well-defined outlines and convex surfaces. This action is often so rapid that it requires a quick eye to follow all the changes.

FIG. 26.



Now it appears that every liquid has its own peculiar figure, by which it, indeed, may often be easily distinguished from other liquids. These figures are usually *more* or *less* permanent, according as the liquid under trial is *less* or *more* soluble in water. The more soluble the liquid, the more quickly does the figure disappear. The figure of kreasote will last for five minutes; that of ether, or of alcohol, but for the fraction of a second. These figures are often extremely beautiful; they are usually altered when two liquids are mingled with each other; and, in many cases, a practised eye can, by the form of the figure produced, detect with certainty the nature of the substance which has been added to the original

* The best way to secure this is to rinse out a glass, to ordinary appearance clean, with a few drops of oil of vitriol, or with a strong solution of caustic potash, which must be allowed to flow over the entire surface, then to wash the glass out with abundance of clean water, not touching the inside either with the fingers or a cloth.

liquid. Indeed, it appears to be very probable that this fact may be extensively useful, as affording a rapid means of judging approximately of the purity of such bodies as the essential oils, many of which are often largely adulterated with the fixed oils, or still more often with oil of turpentine. Fig. 27

Fig. 27.

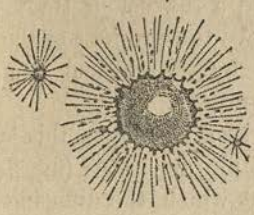
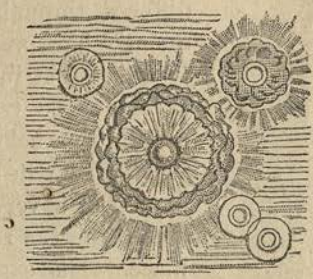


Fig. 28.



shows the appearance exhibited by kreasote; fig. 28, of pure ether; fig. 29, of alcohol. Indeed the films of fixed oils also have characters perfectly distinguish-

Fig. 29.

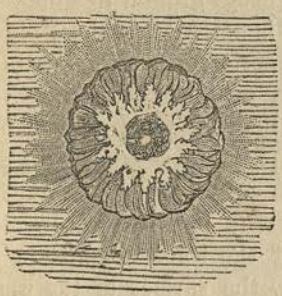
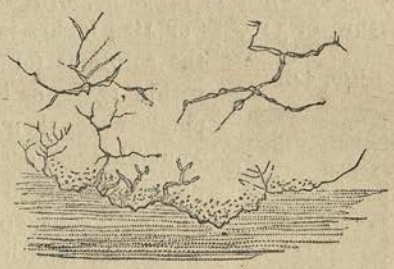


Fig. 30.



able. Sperm, fig. 30, and colza, fig. 31, each have their own cohesion figures; and Tomlinson considers that it would be easy for any one to detect a mixture of the two by the appearance of the film produced by a drop of such a mixture, the result being such as is shown in fig. 32.

Fig. 31.

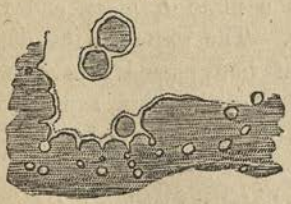
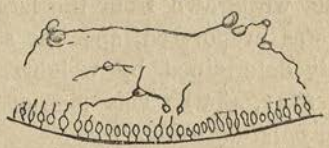


Fig. 32.



(58) *Diffusion of Liquids.*—If two liquids susceptible of permanent admixture with each other, but of different densities, be placed in the same vessel, they will gradually become intermixed:—if, for instance, a tall jar be filled with the blue infusion of

litmus for about two-thirds of its capacity, and by means of a long funnel, as shown in fig. 33, a quantity of oil of vitriol be cautiously poured in, so as to occupy the lower portion of the jar, it will be found, after the lapse of two or three days, that the acid has become diffused through the liquid, which will consequently have assumed a red colour throughout. If watched at intervals, the progress of the mixture may be traced by the gradual change of colour from below upwards.

Fig. 33.

Graham in his researches upon this subject employed a very simple apparatus (fig. 34), for measuring the rate at which the diffusion takes place. His experiments were performed principally upon solutions of saline bodies, which were allowed to diffuse into water. A number of small phials of equal capacity (about 114$^{c.c.}$ or 4 oz. each), were prepared, with the necks ground to a uniform aperture of 31·5$^{mm.}$ or 1·24 inches in diameter; into these phials the solutions for experiment were poured, to within 13$^{mm.}$ or half an inch of the top; the phials were then filled up with pure water. Thus charged, each phial was closed by a glass plate, and placed in a cylindrical vessel containing about 20 oz. (0·567 litre) of distilled water, the mouth of the solution phial being at least 25$^{mm.}$ below the surface of the water in the exterior vessel. The glass plate was then cautiously removed. The apparatus was afterwards set aside in an undisturbed place, and maintained at a steady temperature for several days. After a sufficient lapse of time, the mouth of the solution phial was again closed with a plate of glass, and the vessel withdrawn from the larger jar. The water in the outer jar was evaporated, and the salt that had passed into it was easily determined by weight. (*Phil. Trans.* 1850, 1 and 805, and 1851, 483.) This plan of procedure is distinguished by the term *phial-diffusion.*

Fig. 34.

In his more recent experiments Graham adopted the method of *jar-diffusion*:—In these a cylindrical jar of about 16 centimetres in height and 10 centimetres in width was employed: 0·7 litre of distilled water was placed in the jar, and then by means of a pipette terminating in a very fine capillary tube, 0·1 litre of the solution for diffusion was added slowly so as to form a stratum at the bottom of the jar. The jar was then set aside for some days in an apartment maintained

at a constant temperature. At the end of the time the rate of diffusion was ascertained by drawing off successive layers of the liquid in the jar by means of a fine syphon. The open end of the short limb of the syphon was kept in contact with the surface of the fluid, and successive measures of 50 cub. centim. (or $\frac{1}{16}$ of the whole contents of the jar) were drawn off into separate vessels and evaporated or analysed. In this way the amount of diffusion into each successive layer of liquid was ascertained.

(59) *Laws of Diffusion of Liquids.*—From experiments conducted upon this principle several important conclusions have been deduced:—

i. It is found that by employing solutions of the same substance, but of different degrees of strength, the quantities of the substance diffused in equal times, are, *cæteris paribus*, proportioned to the quantity in the solution. For example, four different solutions of common salt, in water, were prepared, containing respectively, 1, 2, 3, and 4 parts of salt to 100 parts of water. In eight days' time the quantities diffused were, in the first solution, 2·78 grains; in the second, 5·54 grains, or just double the amount; in the third, 8·37 grains, or three times the quantity; and in the fourth, 11·11 grains, or almost exactly four times the amount diffused from the first solution.

ii. No direct relation is observable between the density of a solution and its diffusibility, but the quantities of the substance diffused from solutions containing equal weights of different bodies vary with the nature of the substance, as will be seen by reference to the following table. The solutions in each case contained 20 parts of the solid, dissolved in 100 parts of water, and were exposed for eight days at a temperature of 16° C.

Diffusibility of Solids in Solution.

Substances used.	Density of solution at 16° C. or 60° F.	Weight in grains diffused.
Sodic Chloride...	1·1265	58·68
Magnesic Sulphate	1·185	27·42
Sodic Nitrate	1·120	51·56
Sulphuric Acid	1·108	69·32
Sugar Candy	1·070	26·74
Barley Sugar	1·066	26·21
Starch Sugar	1·061	26·94
Treacle (of Cane Sugar)... ...	1·069	32·55
Gum Arabic	1·060	13·24
Albumin	1·053	3·08

The extreme slowness with which albumin becomes diffused is remarkable; and is no doubt connected with its functions in the

animal system, where it is present so abundantly in the serum of the blood and in other important liquids.

On comparing together the times in which different substances are diffused in equal quantities, some remarkable numerical relations were discovered, and a close parallelism was observed to hold between the phenomena of liquid diffusion and those which accompany the diffusion of gases (67).

It has been found that saline substances may be arranged in groups, the members of each group being equi-diffusive, and the rates of diffusion in each group being connected with the rate of diffusion of the other groups by a simple numerical relation. Equi-diffusive groups coincide in many cases with isomorphous groups, but are often more comprehensive. The relations of the most important of these equi-diffusive groups may be pointed out, as follows :—

The first group contains hydrochloric, hydriodic, and hydrobromic acids; perhaps also nitric acid. These acids are the most diffusible substances known. The second group contains potassic hydrate, and probably ammonia. The third group, nitrates of potassium and ammonium, chloride, bromide, iodide, and chlorate of potassium, and chloride of ammonium. The fourth, sodic nitrate, chloride, bromide, and iodide. The fifth, potassic sulphate, carbonate, and ferrocyanide, as well as ammonium sulphate; probably also the normal and acid chromate, acid carbonate, acetate and ferricyanide of potassium. The sixth group contains sodic sulphate and carbonate; and the seventh, magnesic and zincic sulphates. The nitrates of barium, strontium, and calcium also form an equi-diffusive group.

On comparing together the *squares of the times* in which equal quantities of these different salts are diffused, these numbers exhibit a very interesting ratio to each other, which is illustrated by the following table. In the first column of figures the relative diffusibility of the different groups is given as compared with the hydrochloric acid group; the second shows the times required for the diffusion of equal weights of the individuals composing each group; and in the third is shown the ratio of the squares of those times of equal diffusion.

Ratio of Liquid Diffusion.

Groups.	Rate of Diffusion.	Times of equal Diffusion.	Ratio of Squares of times of = Diffusion.
1. Hydrochloric Acid	1·000	1·000	1
2. Potassic Hydrate	0·800	1·250	1·62
3. Potassic Nitrate	0·565	1·770	3·24
4. Sodic Nitrate	0·462	2·154	4·75
5. Potassic Sulphate	0·400	2·500	6·25
6. Sodic Sulphate...	0·326	3·067	9
7. Magnesic Sulphate	0·200	5·000	25

It has been observed that in the case of gases (67), the squares of the times required for the diffusion of equal volumes are to one another in the inverse ratio of their densities. And hence it has been inferred by analogy that the molecules of these salts *as they exist in solution*, possess densities which are to each other as the squares of their times of equal diffusion: that, for example, the *solution densities* of hydrochloric acid, potassic hydrate, and potassic nitrate, are as 1 : 1·62 : 3·24.

All experiments on the diffusion of liquids proceed with greater regularity in dilute solutions: as the liquid approaches the point of saturation the uniformity of action is interfered with, by the tendency to cohesion of the particles of the solid.

iii. The quantity of any substance diffused from a solution of uniform strength increases as the temperature rises: for example, the rate of diffusion of hydrochloric acid increases as follows:—

F.	C.		
Diffusion at 60°	15°·55	=	1
„ 80°	26°·66	=	1·3545
„ 100°	27°·77	=	1·7732
„ 120°	48°·88	=	2·1812

Graham supposed from his early experiments that the ratio of diffusion between different bodies, if compared at the same temperature, remains constant, whatever the temperature at which the comparison is made; but subsequent experiments led him to the conclusion, that the more highly diffusive the substance, the less does it gain in diffusiveness by rise of temperature.

iv. It is found that if two substances which do not combine chemically, and which possess different degrees of diffusiveness, be mixed in solution, and be placed in a diffusion cell, they may be partially separated by the process of diffusion, the more diffusible one passing out the more rapidly; the salt which is least

soluble having, however, its diffusiveness somewhat reduced in proportion to the other. Upon this fact Graham observes, 'The mode in which the soil of the earth is moistened by rain is peculiarly favourable to separations by diffusion. The soluble salts of the soil may be supposed to be carried down together, to a certain depth, by the first portion of rain which falls, while they afterwards find an atmosphere of nearly pure water in the moisture which falls last, and occupies the surface stratum of the soil; diffusion of the salts upwards, with its separations and decompositions, must necessarily ensue. The salts of potash and ammonia, which are most required for vegetation, possess the highest diffusibility, and will rise first. The pre-eminent diffusibility of the alkaline hydrates may also be called into action in the soil by hydrate of lime, particularly as quicklime is applied as a top-dressing to grass lands.'

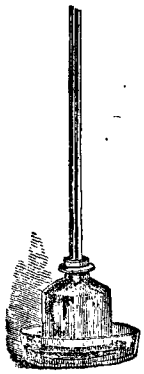
In some cases even chemical decomposition may be effected by the process of liquid diffusion. Thus, if a solution of ordinary alum (which is a compound of potassic and aluminic sulphates in fixed proportions) be placed so as to become diffused into water, the potassic sulphate will pass out more rapidly in proportion to the quantity present than the aluminic sulphate.

v. Provided that the liquids be dilute, it appears that one substance will become diffused into water already containing another body in solution, just as into pure water; but the rate is materially reduced if a portion of the diffusing substance be already present in the surrounding liquid.

In comparing with these the phenomena of gaseous diffusion (67), it will be seen how closely all these points coincide in the two cases.

(60) *Osmose.*—Intimately connected with the process of liquid diffusion are the changes which occur when the two liquids are separated by the intervention of a porous diaphragm. The phenomena here are, however, more complicated, from the part exercised upon the result by the adhesion of the two liquids to the material of the diaphragm. The process of mixture will go on in this case notwithstanding the direct opposition of gravitation.

FIG. 35.



The following experiment exhibits this fact in a striking manner:—Provide a funnel, or a small jar (fig. 35), open at top and bottom, and furnished with a long, narrow stem: over the open mouth of the jar tie a piece of moistened bladder; fill the jar and a portion of the stem with spirit of wine (or with a solution of sugar in water), then place the jar, with its broad

end downwards, in a shallow vessel containing water, noting the height at which the spirit or the solution stands in the stem. In the course of a few hours the column of liquid will be found to have increased in height, and if sufficient time be allowed, it will have risen to the top of the tube, and will at length overflow. This phenomenon has been explained in the following manner:—

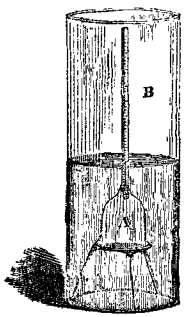
Owing to its greater adhesion to water than to spirit, the bladder is easily moistened by the water in contact with its lower surface, whilst the spirit above wets the bladder with difficulty; the water rises into the bladder by capillarity, and fills its pores; it thus reaches the upper surface, where it comes into contact with the spirit; a true liquid diffusion of the water through the spirit then commences (owing to the combination between the two liquids); a fresh portion of water rises from below into the pores of the bladder to supply the place of that which has been removed, and thus the liquid within the funnel is constantly increasing in bulk, until at length, even in opposition to gravity, the liquid overflows; this *flowing in* of the liquid was termed by Dutrochet, who first particularly examined it, *endosmosis* (from ἔνδον, inwards, and ὦσμὸς, impulse). At the same time that this action proceeds from without inwards, a very small quantity of spirit is *passing out* by a similar process into the water below, and this flowing out of the vessel is designated *exosmosis*. Upon this view the conditions essential to the phenomenon are the more complete adhesion of the bladder to one liquid than to the other, and the existence of a certain degree of chemical attraction between the two liquids. Whenever these conditions are realized, no matter what the liquids may be, the liquid which most freely wets the membrane passes out more rapidly than the other passes in. If a film of collodion, which is more easily wetted by alcohol than by water, be substituted for the bladder in the foregoing experiment, the direction of the osmose will be reversed, and the alcohol will pass into the water more rapidly than the water into the alcohol.

The foregoing explanation, although it is probably true for the particular experiment with alcohol and water, is however inadequate to explain the phenomenon generally, which is one of continual occurrence, and is of importance, especially when viewed in its physiological bearings: the investigations of Graham (*Phil. Trans.* 1854, 177) have also proved it to possess considerable interest in a purely chemical sense.

(61) *Conditions of Osmose.*—The *osmometer* used in these experiments is represented in fig. 36. It consists of a bell-jar, A, of a capacity of 5 or 6 ounces (from 150 to 200 cub. centimetres), over the open mouth of which a plate of perforated zinc is placed, and over this is securely tied a piece of fresh

ox bladder with the muscular coat removed, or else an artificial membrane formed by calico soaked in white of egg and dipped into boiling water to coagulate it; to the upper aperture of the bell-jar, a tube, one-tenth of the diameter of the lower opening of the jar, is fitted. This tube is open at both ends, and is graduated into millimetres. A rise or fall of liquid in the narrow tube amounting to 100 millimetres therefore represents the entrance or removal of a stratum of liquid of 1 millimetre in thickness over the whole surface of the membrane. In using the instrument, the membrane is well macerated in pure water, and the saline solution introduced into the jar, A, until it stands at a fixed mark in the narrow tube. The apparatus is then placed on a tripod stand in a tall cylindrical jar, B, and distilled water poured in until it stands exactly at the level of the liquid in the tube. During the whole experiment this level is carefully maintained, by the addition or removal of water in the outer jar, as circumstances require.

FIG. 36.



The principal points which were ascertained by experiments conducted in this way were the following :—

i. Neutral organic substances, such as urea, gum arabic, sugar of milk, gelatin, and salicin, exercise little or no osmotic action.

ii. Strictly neutral salts, such as magnesic sulphate, sodic chloride, and baric chloride, exercise no peculiar osmotic power, but appear to follow nearly the same rate of diffusion as that which is observed when no porous partition is used.

iii. Alkaline solutions, and especially the solutions of the potassic and sodic carbonates, on the contrary, produce endosmosis to a most remarkable extent. This effect is observed even in solutions which contain not more than 1 part of the salt to 1000 of water. Indeed, it was found generally that these osmotic phenomena were most strongly developed in dilute solutions, such, for instance, as did not contain more than 2 per cent. of the salt. In these experiments a large bulk of water entered the osmometer whilst only a very small portion of the alkaline salt escaped into the water of the outer jar. For example, in 5 hours, when a solution of potassic carbonate containing 1 part of the salt in 1000 of water was placed in the osmometer, the liquid in the stem of the instrument rose through 192 divisions; and for each milligramme of potassic carbonate that became diffused into the outer cylinder, upwards of 550 mgrms. of water entered the osmometer; but when a solution which contained 1 per cent. of potassic carbonate was used, not much more than 63 mgrms. of water entered the instrument for each milligramme of carbonate that became diffused into the outer cylinder. When the liquid *rises* in the osmometer, Graham distinguishes it as *positive osmose.*

iv. On the other hand, dilute acids, and solutions of acid salts generally, produce a current in the opposite direction; consequently the column falls in the stem of the osmometer. This effect is distinguished as *negative osmose*.

Salts which admit of division into a basic salt and free acid exhibit osmotic properties in a high degree. This is well seen in the case of aluminic acetate, plumbic nitrate, zincic chloride, and the chromic and ferric salts. The acid travels outwards by diffusion, and the inner surface of the membrane is left in a basic condition, whilst the outer surface is acid—conditions highly favourable to rapid positive osmose.

v. In every instance in which osmotic action is observed (except in the cases of alcohol and cane sugar), a chemical action on the material of the septum, whether it consists of bladder or of earthenware, invariably occurs; and it is remarkable, that if porous materials, not susceptible of decomposition by the liquids, be made use of as a partition, the osmotic phenomena become insignificant:—for instance, a plug of gypsum, of washed unbaked clay, of tanned leather, or of compressed charcoal, although sufficiently porous, gives rise to little or no osmotic action. To induce osmose under the most favourable circumstances, the chemical action on the septum must be different on the two sides, not only in degree, but also in kind; such as is produced by the presence of acid upon one surface, and of alkali on the other, and the septum itself must belong to the class of colloids (62). These circumstances are specially interesting from their chemical bearings, as is also the next point, which is no doubt connected with the influence of the colloid employed as the septum.

vi. Two salts, when mixed, often have an osmotic action very different from that which they exercise separately. For example, perfectly neutral potassic sulphate has a feeble positive osmose, represented by a rise of $20^{mm.}$ in 5 hours. The addition of 1 part of potassic carbonate to 10,000 of the solution raised it to nearly $100^{mm.}$ in 5 hours, whilst an equally minute trace of hydrochloric acid stopped the osmose almost entirely. Similar results were obtained with sodic sulphate. Sodic chloride, on the other hand, exhibits a remarkable power of reducing osmotic action in other salts. The osmose of a solution of sodic carbonate, containing $\frac{1}{1000}$ of the carbonate, was reduced from $179^{mm.}$ to $32^{mm.}$, by the addition of 1 per cent. of sodic chloride. From other experiments, it appears further that two different saline solutions, one placed in the osmometer, the other in the outer

jar, each solution holding equal weights of the different salts dissolved in the same bulk of water, may also give rise to osmotic action, when separated by a suitable porous partition.

Liebig has shown that the mechanical force of the osmotic current may be measured by the following simple means:—Let the open extremity of the shorter limb of a glass tube bent into the form of a syphon be closed by a piece of bladder, pour a little mercury into the bend of the tube, and fill the shorter limb with the saline liquid under experiment; immerse the bend of the tube and the membrane in water, leaving the extremity of the longer limb open: as the water enters the tube, the mercury will be raised in the longer limb, and when the column reaches a certain height, the two liquids will intermix without change of volume. The length of the column which has been raised above the level of the surface of the mercury in the shorter limb must be measured, and when compared with the length of the column obtained with other liquids under similar circumstances, it offers a comparative measure of the osmotic force for each. Osmotic action thus offers an interesting case of the direct conversion of chemical attraction (on the septum) into motive power, the extent of which admits of ready numerical expression.

Osmotic phenomena are constantly going on both in plants and in animals; for in their tissues, liquids of very different natures, sometimes acid, still more often alkaline, are circulating through vessels necessarily constructed of flexible and porous materials; and in the economy both of the vegetable and of the animal creation such actions are of the highest importance to the due performance of the vital functions. In fact, we as yet know not how intimately the entire processes of absorption, nutrition, and secretion are connected with the operations of liquid diffusion and of endosmosis.

(62) *Dialysis—Crystalloids and Colloids.*—In a subsequent memoir (*Phil. Trans.* 1861, 183), Graham has pursued the subject of liquid diffusion, and applied the process to the purposes of chemical analysis. The most remarkable conclusion at which he arrives in this memoir is that all bodies are chemically referable to one or other of two great classes, which he distingushes as *crystalloids* and *colloids.* Bodies susceptible of crystallization, or *crystalloids,* form a solution generally free from viscosity, and they are always sapid; they are especially endowed with the tendency to diffusion through a porous septum: whilst the *colloids,* or jelly-like substances (from κόλλη, glue), such as gum, starch, dextrin, tannin, gelatin, albumin, and caramel, are charac-

terized by a remarkable sluggishness and indisposition to diffusion or to crystallization; when pure, they are also tasteless or nearly so.

Magnesic sulphate, for instance, one of the least diffusible crystalline bodies, has a diffusibility 7 times as great as that of albumin, and 14 times as great as that of caramel, if compared by determining the relative weights which are diffused in equal times under similar circumstances.

If we compare together the times required for the diffusion of equal weights of different substances, calling the time of hydrochloric acid, the most diffusible of known bodies, unity, the following table may be formed of

Approximate Times of Equal Diffusion.

Hydrochloric acid	1
Sodic chloride	2·33
Cane-sugar	7
Magnesic sulphate	7
Albumin	49
Caramel	98

In making these experiments, some insoluble colloid, such as a sheet of the paper modified by sulphuric acid, which is well known under the name of 'parchment paper,' is employed as a septum through which the diffusion may take place. A ready *dialysis* (from διὰ, asunder, λύσις, separation), or separation of crystalloid and colloid bodies, may be effected in the following manner:—Prepare a shallow tray by stretching a sheet of parchment paper over one side of a hoop of gutta percha; place the mixture for experiment in the tray, and then float it in a shallow dish of pure water, the volume of the water being from 4 to 10 times that of the mixture. In the course of 24 or 48 hours, the separation will have taken place more or less completely. In this way a solution of arsenious acid, for instance, after admixture with various articles of food, readily diffuses out. If the diffusate be evaporated down to a small volume, the arsenious acid may be obtained nearly free from organic matter, and sufficiently pure to yield a yellow precipitate with sulphuretted hydrogen.

The process of dialysis has already received important applications both in pharmacy and in the laboratory. In the examination of organic mixtures for poisons, it affords a simple method of separating almost all crystalline bodies, such as the mineral poisons and the vegetable alkaloids, from the mass of organic

fluids without introducing any extraneous substance, thus leaving the mixture perfectly fit for other modes of examination.

By dialysing solutions of salts of aluminium, chromium, and iron, the hydrates of the metals remain in the soluble condition, the crystallized acids having been separated. When a solution of an alkaline silicate to which an excess of dilute hydrochloric acid has been added is treated in a similar manner, the sodic chloride and free hydrochloric acid are removed and the silicic acid remains in the soluble colloid condition. The solutions of aluminic, ferric, and chromic hydrates and silicic acid thus obtained in the colloid condition are very unstable, showing a great tendency to gelatinize, a change which is hastened by heat, and by the addition of certain salts. A solution containing $\frac{1}{10000}$th part of any alkaline or earthy carbonate effects the coagulation of the colloid silicic acid in a few minutes, and a few drops of well water, caused the gelatinization of a solution containing 2 or 3 per cent. of alumina.

Many colloidal bodies of organic origin, such as gum, albumin, or caramel, may in a similar way be freed from saline impurities, which it is very difficult, if not impossible, to remove by other means. Diffusion, indeed, takes place very perfectly from solid hydrated colloids; this may be shown in a striking manner by the following experiment:—

Let 10 parts of common salt and 2 of gelose, or Japanese gelatine, be dissolved in hot water, which must be added till it forms 100 parts of solution. If this be poured into a glass jar, it will set, on cooling, into a firm jelly; now pour upon this 700 parts of a similar solution of gelose, but containing no sodic chloride; this also will set into solid jelly. In an experiment made in this way, the whole was left undisturbed for eight days, and the result was compared with a similar experiment, in which diffusion of the salt was allowed to take place into an upper stratum of water instead of one of gelose. The rate of diffusion was found to be nearly the same in the two cases, but rather the more rapid in the case of the solid jelly. This process may be watched very readily by substituting a coloured salt, such as cupric sulphate, or potassic dichromate, for sodic chloride.

Graham has suggested the following explanation of the process of dialysis:—The water in the colloidal septum is not *directly* available as a medium for diffusion, being in a state of true chemical combination, feeble though it be. Soluble crystalloids, however, can separate water, molecule after molecule, from the hydrated colloid constituting the septum; the crystalloid in this manner obtains the liquid medium required for its diffusion, and thus makes its way through the gelatinous septum.

Graham indeed supposes that the coats of the stomach dialyse the food during digestion, absorbing the crystalloids and rejecting

all the colloids, an action favoured by the thick coating of mucus which generally lines the stomach. This suggestion probably requires some limitation; otherwise starch, gelatin, and other colloids, unless previously converted into crystalloids, would be wholly unabsorbed after they have been swallowed. The process of dialysis, though most commonly exhibited in animal and vegetable textures, is not confined to them. For example, the cementation of iron, or the process of its slow carburation during its conversion into steel, is supposed to be due to colloid diffusion, the pasty condition to which iron is reducible at a certain elevation of temperature being referred by Graham to its assumption of the colloidal form.

Colloid bodies do not necessarily belong to the organic kingdom, though they are most frequently met with amongst its constituents; and owing to their tendency to undergo slow but perpetual molecular change, together with their peculiar relations to water, they seem to be especially suited to form the plastic materials required for building up the tissues of the living organism.

Indeed, the crystalloid appears to be the static, whilst the colloid is the dynamic condition of a body; and the usual tendency of the colloid is gradually to approach the crystalloid form.

The chemistry of a body in the colloid condition is very different from that of the same body in its crystalloid form. Hydrated or gelatinous silicic acid, soluble alumina, a particular soluble form of hydrated ferric oxide, and of chromic oxide, are instanced by Graham as belonging to the class of inorganic colloids. Each of them, in this state, possesses properties quite different from those which it exhibits in its ordinary or crystalline form. Some colloids are soluble in water, as gelatin and gum arabic; some are insoluble, like gum tragacanth: some form solid compounds with water, as for example, gelatin and tragacanth; whilst others, like tannic acid, do not. In colloids *water of gelatinization* appears to represent in some measure the water of crystallization in crystalloids. Colloids, though often largely soluble, are held in solution by a very feeble force. Fluid colloids appear always to have a gelatinous or *pectous* condition, and they easily pass from the liquid to the gelatinous state.

The combining proportion of colloids is generally high, although the ratio between the elements of the substance may be simple, and it seems not to be improbable that the grouping together of a number of crystalloid molecules may be one of the essential requisites for the development of the colloid condition.

(63) *Flow of Liquids through Capillary Tubes.*—An interesting and close connexion exists between the subjects which have just been considered and *liquid transpiration*, or the flow of liquids through capillary tubes. The most extensive and complete set of experiments hitherto made upon this branch of research is due to Poiseuille. (*Ann. Chim. Phys.* 1847 [3], xxi. 76.)

FIG. 37.

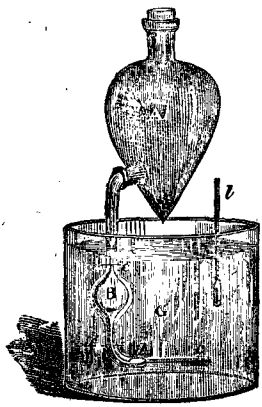


Fig. 37 will explain the method of conducting these experiments: A is a hollow conical metallic vessel which can be attached by a screw joint to a capacious receiver of condensed air, the exact pressure of which can be regulated by means of a gauge attached to it; B is a glass globe, of about half a cubic inch ($8^{c.c.}$) in capacity, which contains the liquid under experiment; it is connected with the metallic vessel, A, by a glass tube of narrow bore. A similar tube proceeds from the lower part of the globe, and to this is attached the capillary tube, *c*, the diameter and length of which are carefully determined. The object of the little bulb, *d*, is merely to enable the observer accurately to define the termination of the capillary tube. G is a vessel which is filled with water, provided with an accurate thermometer, for observing and regulating the temperature. When an experiment is to be made, the end of the capillary, *c*, is introduced into the liquid, and the globe, B, is filled by attaching it to an exhausting syringe. When the liquid has risen a little above the line, *e*, the syringe is detached, and the apparatus connected with the vessel of condensed air. The pressure of this confined air continues without appreciable change during the experiment. By opening a stop-cock, the condensed air exerts its pressure upon the liquid, which is expelled through the capillary tube, *c*, and the column descends in the tube *e f*. By means of a stop-watch, the time at which it reaches the line, *e*, is exactly noted, and the time is again observed when the globe has become emptied, and the liquid has reached the lower line *f*. The object of the conical metallic vessel, A, is to act as a trap or lodging place for any particles of dust that might be suspended in the compressed air, and which, by obstructing the capillary tube, would mar the result.

From the inquiries of Poiseuille, it appears that when a tube exceeds a certain length (which is greater as the diameter increases), the following laws regulate the rate of efflux of the liquid:—1. That the flow increases directly as the pressure; so that, with a double pressure, double the amount of liquid is discharged in equal times. 2. That with tubes of equal diameter, and under equal pressure, the quantities discharged in equal times are inversely as the length of the tube: if from a tube 1 decimetre in length, 10 grammes escape in five minutes, from a similar tube, 2 decimetres long, only 5 grammes would flow out in the same time. 3. That in tubes of equal lengths, but of different diameters, the flow is as the fourth powers of the

diameters; for example, if tubes, one of 0·4 millimetre, another of 0·2 millimetre in diameter, be compared together, the efflux from the larger tube would be 16 times as great as from the smaller, being in the proportion of $2^4 : 4^4$, or as 1 : 16, although the diameter of the tube is only twice as great.

To the chemist, however, the most interesting part of these experiments is that which displays the effect produced by varying the kind of body which is allowed to flow through the capillary tube. The material of which the tube itself is made does not appear to influence the result; but the nature of the solution employed exercises the most marked effect. The liquids used were, in most cases, solutions in water of various bodies, especially of salts. In the majority of instances the flow of the solution was slower than that of distilled water. All the alkalies occasioned this retardation. In a few cases no sensible effect was produced. Thus, neither argentic nitrate, corrosive sublimate, sodic iodide, ferrous iodide, nitric, hydriodic, bromic, nor hydrobromic acid seemed to have any influence; whilst the hydrosulphuric and hydrocyanic acids, and a few of the salts of potassium and ammonia—viz., the nitrates and chlorides of potassium and ammonium, the iodide, bromide, and cyanide of potassium—increased the rapidity of the flow: but it is remarkable that concentrated solutions of potassic iodide above a temperature of 60° C., and of potassic nitrate above 40° C., actually flow more slowly than distilled water does. Strict attention to the temperature at which these comparisons are made is absolutely necessary, for both with water and with dilute solutions generally, a slight elevation of temperature produces a great increase in the rapidity of efflux. Water, for instance, at 45° C., escaped through the same tube with a rapidity of 2½ times as great as it did at 5° C.

Hitherto no connexion has been traced between the rate of efflux of the liquid and its density, capillarity, or fluidity. The capillarity of alcohol, as well as its density, increases as it is diluted with water, whilst its fluidity diminishes; but experiment has proved that a mixture of equal parts of spirit of wine and water flows out with considerably less than half the rapidity of pure alcohol, and with less than one-third of that of distilled water. The dilution of alcohol, therefore, to a certain point, retards its efflux, and beyond that point increases it: the minimum ate of efflux corresponds with that particular mixture of alcohol and water, which is attended with the maximum of contraction after admixture of the two liquids. The degree of solubility of a

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body in water appears to exercise but a secondary influence on the phenomenon. Poiseuille shows it to be highly probable that the various solutions, when introduced into the blood of a living animal, provided that they do not cause the serum to coagulate, produce effects of acceleration or retardation on the capillary circulation, corresponding with those which are observed with the same liquids in capillary tubes of glass. He has proved this to be the case by direct experiment with potassic iodide when injected into the veins of the horse; and has shown that when various salts are mingled with serum, and the liquids are allowed to flow out through small tubes, retardation or acceleration occurs, as in the corresponding cases with their aqueous solutions.

Efflux of Liquids through Fine Tubes.

	Temperature 52°·16 F. (11°·2 C.)					53°·24 F. (11°·8 C.)	53°·42 F. (11°·9 C.)
Distilled Water.	575″·8					566″·2	565″·0
	Nitrate.	Sulphate.	Phosphate.	Arseniate.	Carbonate.	Oxalate.	Chloride.
Potassium ...	564″·5	578″·9	583″·4	583″·3	588″·3	571″·1	560″·8
Ammonium ...	569·4	582·0	590·2	...	...	574·2	560·9
Sodium	575·9	590·3	588·6	588·0	592·5	578·4	569·4
Lead	577·8						
Strontium ...	578·8						
Calcium	581·2	...	...	...	...	...	571·2
Magnesium ...	583·2	590·5	...	...	...	...	574·9
Alum	...	592·4	Tartar Emetic, 581·2				

Distilled water ...	575″·8	Arsenic acid	586″·3
Arsenious acid ...	578·6	Sulphuric acid ...	589·6
Phosphoric acid ...	582·8	Pure serum, Ox ...	1048·5
Oxalic acid	582·9	Madeira wine ...	1134·1
Acetic acid	585·5	Sparkling Sillery ...	1462·8
Citric acid	586·0	Jamaica rum	1831·9

The preceding table contains several of Poiseuille's results, numerically expressed. The solutions employed contained 1 per cent. of the various substances mentioned, except in the case of the last four liquids. They were exposed to a pressure equal to that of a column of water 1 metre (39·37 inches) in height, at the temperature of 11°·2 C., unless otherwise noted; and escaped through a tube 64 millimetres in length, and 0·24946$^{mm.}$ in diameter. The numbers in the table indicate the time occupied in seconds, for the efflux of equal bulks of the liquids used—viz., 6·6 cubic centimetres.

The observation of Poiseuille, that diluted alcohol has a point of maximum retardation coincident with the degree of dilution at which the greatest condensation of the mixed liquids occurs, or at a point in which 1 molecule of alcohol and 3 of water (C_2H_6O, 3 H_2O) are present in mixture, served as a starting-point to Graham for a new inquiry. (*Phil. Trans.* 1861, 373.) The rate of transpiration he has proved to be, in certain cases, connected with chemical composition. The 3-molecule hydrate of methylic alcohol, although not distinguished by any particular degree of condensation in volume, exhibits a peculiarity in its transpiration-rate similar to that of dilute vinic alcohol. The acids, also, in many cases, exhibit a characteristic retardation of transpiration at a particular degree of hydration.

As a result of his inquiries, Graham also concluded that as far as his observations upon different alcohols, ethers, and acids, extended, the order of succession of individual substances in any homologous series would be indicated by the degree of transpirability of these substances as clearly as it is by their comparative volatility.

The following table contains a *résumé* of some of the most interesting results obtained by Graham upon this subject. The transpiration time of water at the particular temperature employed is, in all cases, taken as the unit of comparison :—

Liquid (undiluted).	Transpiration time.	Degree of Hydration.	Transpiration time.
Water	1·0000		
Methylic Alcohol, CH_4O	0·6300	+ 3 H_2O	1·8021
Vinic Alcohol, C_2H_6O	1·1957	+ 3 H_2O	2·7872
Amylic Alcohol, $C_5H_{12}O$	3·6490		
Ethyl Formiate	0·5110		
Ethyl Acetate	0·5530		
Ethyl Butyrate	0·7500		
Ethyl Valerate	0·8270		
Acetic Acid ($HC_2H_3O_2$)	1·2801	+ H_2O	2·7040
Butyric Acid ($HC_4H_7O_2$)	1·5650	+ H_2O	3·2790
Valeric Acid ($HC_5H_9O_2$)	2·1550	+ H_2O	3·8390
Nitric Acid (HNO_3)	0·9899	+ 1½ H_2O	2·1034
Sulphuric Acid (H_2SO_4)	21·6514	+ H_2O	23·7706
Acetone (C_3H_6O)	0·4010	+ 6 H_2O	1·6040

In hydrated substances, the extent to which transpiration is affected by the annexation of water, is by no means in proportion to the intensity of combination. In sulphuric acid, for instance, the maximum transpiration time occurs with the hydrate (H_2SO_4,H_2O), in acetic acid with the compound ($HC_2H_3O_2$,H_2O),

in nitric acid with ($2\ HNO_3$, $3\ H_2O$), and in alcohol with the hydrate (C_2H_6O, $3\ H_2O$).

(64) *Adhesion of Gases to Liquids.*—The adhesion of gases to liquids, although not quite so evident as that of solids to liquids, is yet attended with results almost equally important. It is exemplified in the pouring of liquids from one vessel to another, by the bubbles which are carried down with the descending stream, and which rise and break upon the surface of the liquid.

Adhesion, however, produces in the effects of solution which attend the mutual action of gases and liquids, results which are far more general in their operation. All gaseous bodies are in a greater or less degree soluble in water: some, as hydrochloric acid and ammonia, being absorbed by it with extreme rapidity, the liquid taking up 400 or 600 times its volume of the gas; in other instances, as occurs with carbonic anhydride, water takes up a volume equal to its own; whilst in the case of nitrogen, oxygen, and hydrogen, it does not take up much more than from a twentieth to a fiftieth of its bulk. As the elasticity of the gas is the power which is here opposed to adhesion, and which at length limits the quantity dissolved, it is found that the solubility of each gas is greater, the lower the temperature, and the greater the pressure exerted upon the surface of the liquid. Dr. Henry found that at any given temperature, the *volume* of any gas which was absorbed was uniform, whatever might be the pressure; consequently that the *weight* of any given gas absorbed by a given volume of any liquid at a fixed temperature increased directly with the pressure. If the pressure be uniform, the quantity of any given gas absorbed by a given liquid is also uniform for each temperature; and the numerical expression of the solubility of each gas in such liquids is termed its *coefficient of absorption*, or *of solubility*, at the particular temperature or pressure; the volume of the gas absorbed being in all cases calculated for 0° C., under a pressure of $760^{mm.}$ of mercury. For instance, 1 volume of water, at 0° C., and under a barometric pressure of $760^{mm.}$, dissolves 0·04114 of its volume of oxygen; and this fraction represents the coefficient of absorption of oxygen at that temperature and pressure. All water contains a certain small proportion of air in solution, in consequence of the solubility of the gases of which the atmosphere consists; and if placed in a vessel under the air-pump, so as to remove the atmospheric pressure from its surface, the dissolved gases rise through the liquid in minute bubbles. Small as is the quantity of oxygen thus taken up by water from

the atmosphere, it is the means of maintaining the life of all aquatic plants and animals; if the air be expelled from water by boiling, and it be covered with a layer of oil to prevent it from again absorbing air, fish or any aquatic animals placed in such water quickly perish. Even the life of the superior animals is dependent upon the solubility of oxygen in the fluid which moistens the air-tubes of the lungs, in consequence of which this gas is absorbed into the mass of the blood as it circulates through the pulmonary vessels.

If a mixture of two or more gases be placed in contact with a liquid, a portion of each gas will be dissolved, and the amount of each so dissolved will be proportional to the relative volume of each gas in the mixture multiplied into its coefficient of solubility at the observed temperature and pressure:—For instance, if it be assumed in round numbers, that atmospheric air contains one-fifth of its bulk of oxygen, and four-fifths of its bulk of nitrogen, the amount of each of these gases which water should absorb from the air at a temperature of 15° C. under a pressure of 760^{mm}, may be calculated in the following manner. The coefficient of absorption for oxygen at 15° C. is 0·02989, that of nitrogen is 0·01478:—

$\frac{1}{5}$ 0·02989 = 0·00597 proportion of oxygen dissolved.
$\frac{4}{5}$ 0·01478 = 0·01182 proportion of nitrogen dissolved.

0·01779 proportion of air dissolved.

The proportion of nitrogen thus required by calculation is rather less than double that of the oxygen, or 66·1 : 33·9, a proportion which agrees almost exactly with the results of experiment.

When water saturated with one gas is brought into contact with another gas, the second gas will gradually expel the first, and if the quantity of this new gas be very large, it may displace the first altogether. Hence it is impossible to preserve gases in a pure condition over water. Every gas is to a certain extent soluble in water, and this solution is perpetually giving out its gas into the atmosphere, and absorbing oxygen and nitrogen from the air, so that these gases become diffused slowly into the jar which confines the gas under experiment. A jar of hydrogen confined over water in the pneumatic trough will thus in a few days become contaminated with atmospheric air, although it may have experienced little apparent change in bulk.

From the experiments of Bunsen, of Roscoe, and others, it appears that Henry's law is exact for the gases of moderate solubility, but the more soluble gases, such as ammonia, hydrochloric

acid, and sulphurous anhydride, except under moderate pressure, and at mean temperatures, do not strictly follow the law. In these instances disturbing causes are evidently at work. In the case of chlorine, for example, at low temperatures a definite crystalline hydrate is formed, so that true chemical attraction conspires to exalt the effect of adhesion. In the solution of the very soluble gases a considerable elevation of temperature occurs, and a great increase in the bulk of the liquid takes place.

The following table shows the solubility of some of the principal gases, both in water and in alcohol, with the barometer at 760^{mm}. (Bunsen, *Liebig's Annal.* 1855, xciii. 1, and Carius, *Ib.* 1855, xciv. 129.) All these gases, with the exception of hydrochloric acid, may be expelled from the water by long-continued boiling:—

Solubility of Gases in Water and in Alcohol.

Gases.	Volumes of each Gas dissolved in 1 Volume Of Water.		Of Alcohol.	
	At 32° F. or 0° C.	At 59° F. or 15° C.	At 32° F. or 0° C.	At 59° F. or 15° C.
Ammonia	1049·60	727·2		
Hydrochloric Acid ...	505·9	458·0		
Sulphurous Anhydride	68·861	43·564	328·62	144·55
Sulphuretted Hydrogen	4·3706	3·2326	17·891	9·539
Chlorine	solid	2·368		
Carbonic Anhydride	1·7967	1·0020	4·3295	3·1993
Nitrous Oxide... ...	1·3052	0·7778	4·1780	3·2678
Olefiant Gas	0·2563	0·1615	3·5950	2·8825
Nitric Oxide	...	...	0·31606	0·27478
Marsh Gas	0·05449	0·03969	0·52259	0·48280
Carbonic Oxide ...	0·03287	0·02432	0·20443	0·20443
Oxygen	0·04114	0·02989	0·28397	0·28397
Nitrogen	0·02035	0·01478	0·12634	0·12142
Air	0·02471	0·01795		
Hydrogen	0·01930	0·01930	0·06925	0·06725

Other liquids besides water and alcohol dissolve the gases with greater or less avidity.

(65) *Adhesion of Gases to Solids.*—When iron filings are gently dusted over the surface of a vessel of water, a considerable body of iron dust may be accumulated upon the surface, until at length it falls in large flakes, carrying down with it bubbles of air of considerable size. The adhesion of these bubbles caused the particles of iron to float, for such particles are nearly eight times as heavy as water. Contrasted with this result is the effect of dusting magnesia in fine powder over the surface of water; the

particles, although not one-third of the density of the iron, immediately become moistened and sink. In consequence of this adhesion of air to their surface, many small insects are enabled to skim lightly over the surface of water, which does not wet them. If a slip of clean platinum be placed in mercury, it is found on withdrawing it to come out dry, but if the mercury be boiled on the platinum, the film of air which separated the two metals is expelled, and the mercury will be found to have wetted the surface completely. It is this adhesion of air to the surface of glass which renders it necessary, in making barometers, to boil the mercury in the tubes after they have been filled, in order completely to expel the film of air, with which the tube is lined. But the most striking instances of adhesion between gases and solids are exhibited when finely-divided bodies are made the subject of experiment. We have already had occasion to notice the effect of charcoal when introduced into solutions (54). Its effects on gases are equally remarkable. If a piece of well-burnt boxwood charcoal be plunged whilst red-hot under mercury, and introduced without exposure to the air into a jar of ammonia or of hydrochloric acid, it will absorb these gases with great rapidity, and will indeed reduce them into a bulk less than that which they would occupy in the liquid form. A piece of freshly-burned charcoal when exposed to the air condenses moisture rapidly within its pores, and has been observed from this cause to increase in weight nearly one-fifth in a few days.

Owing to this property of charcoal, water saturated with many gases may be freed from them when filtered through a body of ivory black: sulphuretted hydrogen may thus be removed so completely, that it cannot be detected either by its nauseous odour, or by the ordinary tests. De Saussure (*Thomson's Annals of Philosophy*, 1815, vi. 243) found that freshly-burned boxwood charcoal absorbed different gases in very different proportions, as will be seen in the following tabular view of his results, where the bulk of the charcoal used in each experiment is taken as 1:—

Absorption of Gases by Charcoal.

Ammonia	90	Olefiant Gas	35
Hydrochloric Acid	85	Carbonic Oxide	9·42
Sulphurous Anhydride ...	65	Oxygen	9·25
Sulphuretted Hydrogen ...	55	Nitrogen	7·5
Nitrous Oxide	40	Marsh Gas	5·0
Carbonic Anhydride... ...	35	Hydrogen	1·75

It will be seen that these results follow an order almost exactly the same as that of the solubility of the gases in water (64).

Different kinds of charcoal vary considerably in this absorbent power. The denser the charcoal the greater is its absorbent power. Hunter found that formed from the shell of the cocoa-nut was the most powerful absorbent of any which he tried, both ebony and logwood charcoal being much inferior. Stenhouse found, on comparing equal weights of three different forms of charcoal, that the relative absorbent power of each was as follows:—

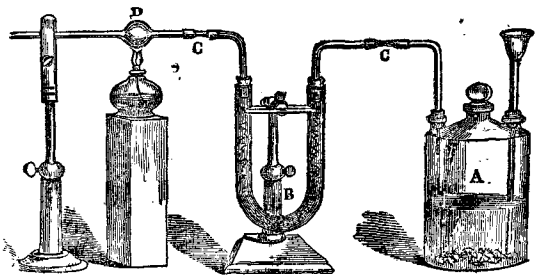
Gas used.	Kind of Charcoal employed.		
	Wood.	Peat.	Animal.
Ammonia	98·5	96·0	43·5
Hydrochloric Acid	45·0	60·0	
Sulphuretted Hydrogen ...	30·0	28·5	9·0
Sulphurous Anhydride ...	32·5	27·5	17·5
Carbonic Anhydride	14·0	10·0	5·0
Oxygen	0·8	0·6	0·5

In these experiments, 0·5 gramme of each kind of charcoal was employed, and the numbers in the table indicate, in cubic centimetres, the quantity of each gas absorbed. The more recent experiments of Hunter and Angus Smith confirm these results. This absorbent action of charcoal renders it a valuable agent in the purification of atmospheric air when contaminated with offensive products of decay or putrefaction, such air being, as Stenhouse has shown, rendered inodorous by simply passing it over fragments of wood charcoal, a true oxidation of many of these bodies being effected in the pores of the charcoal (366).

Charcoal which is saturated with one gas, if put into a different gas, gives up a portion of that which it had first absorbed, and takes up in its place a quantity of the second. Finely divided metallic platinum also condenses in its pores a large quantity of many gases, amounting in the case of oxygen to very many times its own volume. If a jet of hydrogen gas be allowed to fall in the open air upon a ball of *spongy* platinum, or platinum in a fine state of subdivision, the metal becomes incandescent; the oxygen and hydrogen combine rapidly within the pores of the metal, and the heat given out usually sets fire to the jet of hydrogen: ether and alcohol, when dropped upon *platinum black*, another still more finely-divided form of the metal, produce a similar appearance of incandescence. This property of platinum is turned to account in effecting many important chemical changes.

(66) *Desiccation of Gases.*—It frequently happens that in the course of his operations, the chemist requires the gases which are the subjects of his experiments to be in a perfectly dry state. Gases are usually prepared in contact with water, and hence become charged with a variable quantity of aqueous vapour which adheres to them, and whether it be desired to ascertain their density, or to submit other bodies to their chemical influence, it becomes necessary to remove this moisture completely. The gas to be dried, which we will suppose to be in the act of formation in the glass bottle, A, fig. 38, is allowed to pass slowly through a long tube, B, filled with fragments of fused potash, or of calcic chloride, or of quicklime, or of phosphoric anhydride, or of pumice-stone moistened with oil of vitriol, according to the nature of the gas. The bulb, D, may contain the substance upon which the action of the gas is to be exerted, and the gas when it reaches it will be in a dry state; since all the bodies just mentioned possess the property of combining with water and aqueous vapour; and if allowed a sufficient length of time, will remove nearly every trace of moisture from the gases which are brought into contact with them. The different parts of the apparatus are connected by flexible tubes of caoutchouc, c, c.

FIG. 38.



Diffusion of Gases.

The process of intermixture in gases, and the motions of these bodies, have been even more completely investigated than the corresponding processes in liquids. The movements of gases may be considered under four heads; viz.,—

1. *Diffusion,* or the intermixture of one gas with another.

2. *Effusion,* or the escape of a gas through a minute aperture in a thin plate into a vacuum.

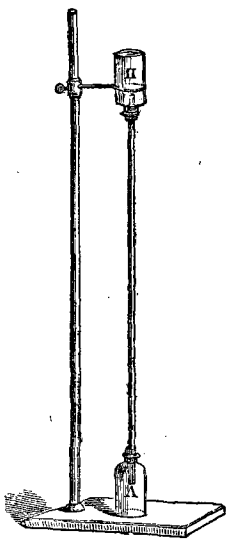
3. *Transpiration,* or the passage of different gases through long capillary tubes into a rarefied atmosphere.

4. *Osmosis,* or the passage of gases through diaphragms.

(67) *Diffusion of Gases.*—In consequence of the absence of cohesion among the particles of which gases and vapours consist,

mixture takes place amongst these bodies very freely, and in all proportions. Very great differences in density occur amongst the gases. Chlorine is, for instance, nearly 36 times denser than hydrogen, the lightest of the gases, so that there is about three times as great a difference between the relative weights of these two gases, as between those of mercury and water. But the mingling together of gaseous bodies of different densities produces a result very different from that obtained by the mingling together of two liquids, such as mercury and water; for, if these liquids be mixed by agitation, they separate the instant that the agitation is discontinued. Chlorine and hydrogen, on the other hand, after they have once become mixed, never separate, however long they may remain at rest. Indeed, if the gases be placed in two distinct vessels, and be allowed to communicate only by means of a long tube, the hydrogen or lightest gas being placed uppermost, as represented at H, fig. 39, the heavier chlorine in A, will, in the course of a few hours, find its way into the upper jar, as may be seen by its green colour, whilst the hydrogen will pass downwards into the lower one, and ultimately the gases will be equally intermixed throughout. If a sufficient interval of time be allowed, this equal intermixture occurs with all gases and vapours which do not act chemically upon each other; and when once such a mixture has been effected it continues to be permanent and uniform. The rapidity with which this *diffusion* occurs varies with the density of the gases; and, contrary to what a superficial consideration might lead us to suppose, the more widely the two gases differ in density, the more rapid is the process of intermixture. If two tall narrow jars of equal diameter be about half filled, the one with hydrogen, the other with common air, which is more than fourteen times as heavy as the hydrogen, so that the water in both shall stand at the same level, and a small quantity of ether be thrown up into each jar, the ether will evaporate in both, and cause in each, ultimately, an equal depression; but the vapour of the ether will dilate the hydrogen at first much more rapidly than the air, for its vapour will become more quickly diffused through the lighter hydrogen. A

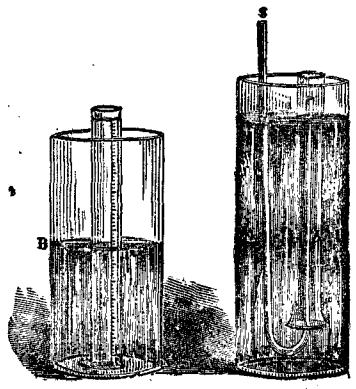
FIG. 39.



very simple and striking illustration of the rapidity with which a light gas becomes diffused into a heavier one, is shown as follows:—

Take a tube 25 or 30 centimetres, or about 10 or 12 inches long, one end of which is closed with a porous plug of plaster of Paris, $5^{mm.}$ thick, that has been allowed to become dry, and fill it with hydrogen gas, without wetting the porous plug: this is readily effected by introducing the shorter limb of an inverted syphon, *s*, into the jar, *b*, fig. 40, till it reaches the top, and then lowering the jar in a deep vessel of water, A; when the air has escaped, the open limb of the syphon is closed with the finger, and the jar raised until the syphon can be conveniently withdrawn: the jar can now be filled with hydrogen prepared in a retort in the usual manner. If the jar after being filled with hydrogen be supported so that the water within and without shall stand at the same level, the water in the jar will immediately begin to rise, and will continue to do so in opposition to gravity, until, in the course of three or four minutes, it will stand some inches higher than the surface of the water in the outer vessel, in consequence of the hydrogen passing through the pores of the stucco, and becoming diffused into the air much more rapidly than the air passes in and becomes diffused through the hydrogen.

FIG. 40.



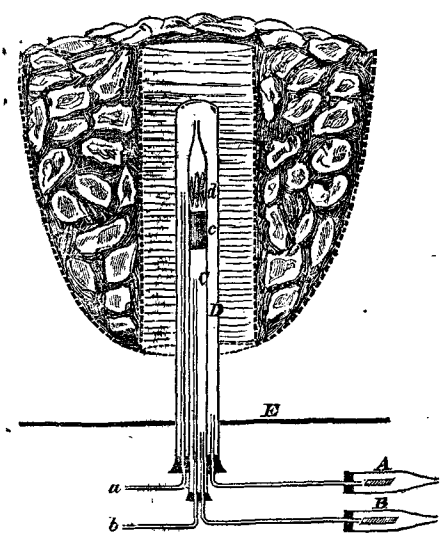
Any dry porous substance may be substituted for the plaster; a film of collodion on paper gives excellent results, and unglazed biscuit-ware, or compressed plumbago, is still better.

By means of this simple diffusion tube, taking care to maintain the surface of the water within and without the jar on the same level, as shown at B, in order that the results may not be interfered with by the disturbing force of gravity, Graham has determined the law which regulates the rapidity of gaseous diffusion. Experiments so made show that the diffusiveness or *diffusion volume* of a gas is in the inverse proportion of the square root of its density; consequently the squares of the times of equal diffusion of the different gases are in the ratio of their specific gravities. For instance, the density of air being 1, the square root of that density is 1, and its diffusion volume is also 1; the density of hydrogen is 0·06926, the square root of that density is 0·26317, and its diffusion volume $\frac{1}{0.26317} = 3{\cdot}7998$; or as actual experiment shows, 3·83; that is to say, in an experiment conducted with due precautions, whilst 1 measure of air is passing into the diffusion tube, 3·83 measures of hydrogen are passing out of it.

In the case where different gases are mixed and then introduced into the diffusion tube, each preserves the rate of diffusion peculiar to itself. If, for instance, hydrogen and carbonic anhydride be mixed and placed in the diffusion tube, the hydrogen passes out with much the greater rapidity: a partial mechanical separation of two gases differing in density may thus be effected.*

* In particular cases advantage may be taken of this fact in the analysis of a mixture of different gases. Suppose it be desired to ascertain whether a certain gas be a mixture, or a single gas—to distinguish, for example, marsh gas ($2\,CH_4$) from a mixture of equal measures of hydrogen, and hydride of ethyl ($H_2 + C_2H_6$)—the two would give exactly similar amounts of carbonic anhydride and water when detonated with oxygen. But suppose that, by eudiometric analysis of a portion of the mixture, the proportions of carbon and hydrogen have been determined, if another portion be submitted to diffusion, and the residue be again analysed, the proportions of carbon and hydrogen will remain unaltered if the gas consist of marsh gas only; whereas, if it be a mixture, the proportion of hydrogen will be diminished. Pebal has ingeniously applied this method to the examination of the question whether the vapours of certain compounds which, like hydrochlorate of ammonia, yield anomalous vapour volumes, are not really, as Cannizzaro supposes, mixtures at those high temperatures, instead of chemical compounds, and he has succeeded in demonstrating the truth of this hypothesis (*Liebig's Annal.* 1862, cxxiii. 199). He places a plug of amianthus (*c*, fig. 41), on which some fragments of sal-ammoniac *d* are supported, within a tube *C*, drawn out to a capillary end: this tube is supported in a wider one *D*, and a current of hydrogen is transmitted through the tubes *a A*, *b B*, which are surrounded by a charcoal furnace, by which they may be sufficiently heated to volatilize the hydrochlorate of ammonia. The vapours of the hydrochlorate being formed in the inner tube, above the plug of asbestos, ammoniacal gas diffuses through the plug into the hydrogen in the tube *C*, and may be demonstrated by causing the issuing gas to come into contact with the reddened litmus paper in *B*; while the hydrogen which traverses the space between the two tubes contains the corresponding hydrochloric acid, and reddens blue litmus in *A*. Hence it is evident that the sal-ammoniac when converted into vapour becomes, partially at least, *dissociated*, as Deville calls it, into its constituents, ammonia and hydrochloric acid, since the ammonia, which is the more diffusible, passes out through the plug the more rapidly of the two.

FIG. 41.



A still more remarkable result may be obtained by the use of an apparatus like the following:—A porous tube, such as the long stem of a tobacco-pipe, is fixed, like the inner tube of a Liebig's refrigerator, by means of perforated corks, within a glass or metallic tube a few centimetres less in length, and about $38^{mm.}$ ($1\frac{1}{2}$ inch) in diameter. A second quill tube is made to pass through one of the corks, and affords the means of communication between the annular space and the vacuum of an air-pump. If a vacuum be maintained in the outer tube, and a current of the mixed gases be transmitted through the tobacco-pipe, a portion of this gas will be drained off; whilst another portion will pass off at the open extremity of the porous tube, and may be collected. The stream of gas diminishes as it proceeds, the more diffusible gas being drained away the most rapidly; and the more slowly the gas is passed though this *atmolyser*, as the apparatus is termed by Graham, the more concentrated does the heavier gas become.

For example, a mixture of 1 volume of oxygen and 2 of hydrogen was transmitted at the rate of 9 litres per hour: 0 45 litre of the mixed gas was collected. Instead of O 33·3, H 66·7, it now contained O 90·7, and H 9·3. It was no longer explosive, but rekindled a glowing match.

Since all gases expand equally (134) by the action of equal additions of heat, their relative densities are preserved, and the relative velocities of diffusion are therefore preserved also, whatever the temperature, provided that both gases be heated equally. The rate of diffusion of equal volumes of different gases becomes, as we might expect, accelerated by a rise of temperature; for by heat all gases are rendered specifically lighter; but the rate of diffusion does not increase so rapidly as the direct expansion of gases by heat. Consequently the same absolute weight of any gas will be diffused more rapidly at a low than at a high temperature.

The process of diffusion is one which is continually performing an important part in the atmosphere around us. Accumulations of gases, which are unfit for the support of animal and vegetable life, are by its means silently and speedily dispersed, so that this process contributes largely to maintain that uniformity in the composition of the aërial ocean which is so essential to the comfort and health of the animal creation. Respiration itself, but for the process of diffusion, would fail in its appointed end, of rapidly renewing to the lungs a fresh supply of air, in place of that which has been rendered unfit for the support of life by the chemical changes which it has undergone.

Graham applied to gases a method resembling that of jar diffusion employed for liquids (58). A glass cylinder of 0·57 metre high (22·44 inches) was filled for the lower tenth of its volume with carbonic anhydride, at 16° C., the remainder being filled with air. The air in the upper tenth of the jar was then examined after the lapse of a certain time for carbonic anhydride. After an interval of five minutes, 0·4 per cent. in one experiment, and in a second 0·32 per cent. of this gas was found in this stratum, and in seven minutes the amount of CO_2 was nearly 1 per cent.; so that it appears that about 1 per cent. of carbonic anhydride will, under these circumstances, become diffused to a

distance of half a metre in seven minutes. On repeating the experiment with a light gas, such as hydrogen, it was found to travel downwards in the same jar about five times as rapidly as the carbonic anhydride ascended; and Graham concludes that the molecules of hydrogen in a gas apparently motionless disperse themselves to the distance of a third of a metre in a single minute (*Phil. Trans.* 1863, 405).

Diffusion and Effusion of Gases.

Gas.	Density.	Square Root of Density.	$\frac{1}{\sqrt{\text{Density}}}$	Velocity of Diffusion. Air=1.	Rate of Effusion.
Hydrogen	0·06926	0·2617	3·7998	3·83	3·613
Marsh Gas	0·559	0·7476	1·3375	1·344	1·322
Steam	0·6235	0·7896	1·2664		
Carbonic Oxide	0·9678	0·9838	1·0165	1·0149	1·0123
Nitrogen	0·9713	0·9856	1·0147	1·0143	1·0164
Olefiant Gas	0·978	0·9889	1·0112	1·0191	
Nitric Oxide	1·039	1·0193	0·9810		
Oxygen	1·1056	1·0515	0·9510	0·9487	0·950
Sulphuretted Hydrogen ...	1·1912	1·0914	0·9162	0·95	
Nitrous Oxide	1·527	1·2357	0·8092	0·82	0·834
Carbonic Anhydride	1·52901	1·2365	0·8087	0·812	0·821
Sulphurous Anhydride ...	2·247	1·4990	0·6671	0·68	

The preceding table gives the density of several important gases, the square root of the density, or ratio of the times required for the diffusion of equal volumes, if the time for air=1, the reciprocal of that square root, or calculated diffusiveness of the gas, and the actual numbers obtained by experiment, when the barometric pressure and the temperature were the same for each gas.—(Graham, *Phil. Mag.* 1833, ii. 352.)

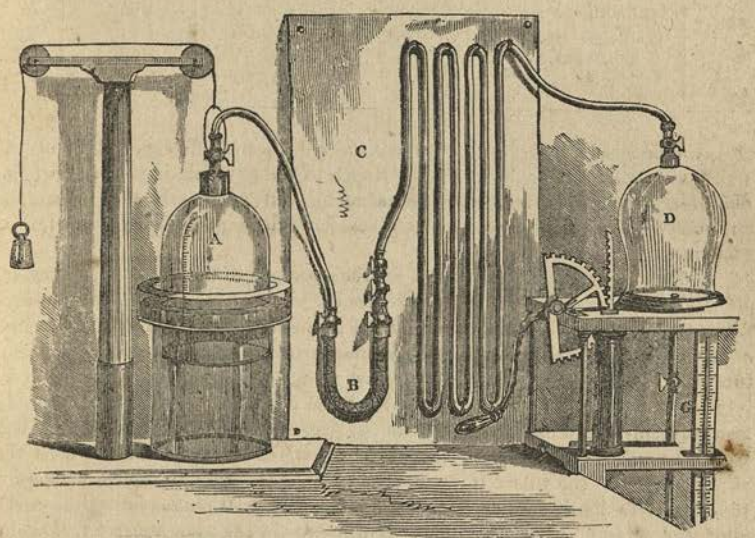
(68) *Effusion.*—The numbers in the last column of the table headed 'Rate of Effusion,' are the results obtained by experiment upon the rapidity with which the different gases escape into a vacuum through a minute aperture, about $\frac{1}{100}$ of an inch ($0{\cdot}086^{mm}$.) in diameter, perforated either in a thin sheet of metal or in glass (Graham, *Phil. Trans.* 1846, 574). It is evident that they coincide, within the limits of experimental errors, with the relative rates of diffusion of each gas; and that the velocities with which different gases pass through the same small aperture into a vacuum, are inversely as the square roots of the densities of the gases. The lightest gas enters the most rapidly. Change in the density of the gas has but little influence on the rate of effusion, the volume effused in a given time being nearly uniform, whatever the amount of condensation or of rarefaction.

The rate of the efflux of liquids, when passing through an aperture in a very thin plate, is found also to be inversely as the square roots of their densities.

On the velocity of effusion of gases Bunsen has founded an elegant method of determining their densities. The gas is introduced into a tube, from which it is allowed to escape through a minute hole in a thin platinum plate, the time occupied by the effusion of a known volume being carefully noted. The experiment is then repeated with air or some gas of known density, and from the numbers obtained the density of the first gas is easily calculated (*Bunsen's Gasometry*, Roscoe's translation, 1857, 121).

(69) *Transpiration of Gases.*—When gases are transmitted through fine tubes, a result very different from that furnished by diffusion is obtained, corresponding with the effect already described in the case of liquids which are allowed to escape through fine tubes. A series of experiments on gases and vapours (Graham, *Phil. Trans.* 1846, 591, and 1849, 349), analogous to those upon liquids by Poiseuille, already described (63), showed that the rate of efflux for each gas or the velocity of *transpiration* (as Graham terms this passage of gas through long capillary tubes), is entirely independent of its rate of diffusion. In the performance of these experiments, the gas was placed over

FIG. 42.



water, in a graduated jar, A, fig. 42, so suspended that the liquid in the jar and in the bath could be readily kept at the same level. The gas was dried, by causing it to pass through a tube, B, filled with calcic chloride, and was then allowed to enter through a long fine capillary tube, C, into the exhausted receiver, D, of the air-pump, which was sometimes kept vacuous by continued pumping; at other times, the state of the exhaustion was ascertained, at intervals, by means of the gauge, G. In all cases, the quantities of gas that entered in a given time were carefully observed.

Transpirability of Gases.

Gases.	Times for Transpiration of Equal Volumes.	Velocity of Transpiration.
Oxygen	1·0000	1·0000
Air	0·9030	1·1074
Nitrogen	0·8768	1·141
Nitric Oxide	0·8764	1·141
Carbonic Oxide	0·8737	1·144
Nitrous Oxide	0·7493	1·335
Hydrochloric Acid	0·7363	1·358
Carbonic Anhydride	0·7300	1·370
Chlorine	0·6664	1·501
Sulphurous Anhydride	0·6500	1·538
Sulphuretted Hydrogen	0·6195	1·614
Marsh Gas	0·5510	1·815
Ammonia	0·5115	1·955
Cyanogen	0·5060	1·976
Olefiant Gas	0·5051	1·980
Hydrogen	0·4370	2·288

It is necessary, in order to overcome the influence of effusion, and to furnish uniform results, to employ a certain length of tube, which increases with the diameter, and is not uniformly the same for all gases. If this precaution be observed, it appears, when the gases flow through capillary tube into a vacuum—

1. That the rate of transpiration for the same gas increases, *cæteris paribus*, directly as the pressure; in other words, equal volumes of air, at different densities, require times inversely proportional to the densities. For example, a pint of air of double the density of the atmosphere will pass through the capillary tube into the vacuum in half the time that would be required for a pint of air of its natural density. This is a very remarkable result, and stamps the process of transpiration with a character quite unlike that of diffusion or effusion. 2. That with tubes of equal diameter, the volume transpired in equal times is inversely as the length of the tube; if 500 cubic centimetres were transpired through a tube 3 metres long, in five minutes, a similar tube, 6 metres in length, would allow the passage of only 250 cubic centimetres in the same time. 3. That as the temperature rises, the transpiration of equal volumes becomes slower. 4. That whether the tubes were of copper or of glass, or whether a porous mass of stucco were used, the same uniformity in the results was obtained. By comparing together different gases under similar circumstances, the rate of transpiration, or rapidity of passage into a vacuum through a capillary tube, was found to vary with the chemical nature of the gas. These velocities of different gases bear a constant relation to each other, totally independent of their densities, or indeed of any other known property of the gases.

Graham considers that it is most probable that the rate of transpiration is the resultant of a kind of elasticity depending upon the absolute quantity of heat, latent as well as sensible, which different gases contain under the same volume; and therefore that it will be found to be connected more immediately with the specific heat than with any other property of gases.

Of all the gases tried, oxygen has the slowest rate of transpiration; and hence that gas may be conveniently taken as the standard of comparison for the other gases, as has been done in the preceding table, which shows the relative times in

which equal volumes of the different gases are transpired, and their relative velocities; these are of course inversely as the times.

A mixture consisting of equal volumes of two gases which differ in their rates of transpiration, does not always exhibit a transpirability the mean of that of the two gases when separate. The transpiration-time of hydrogen is greatly prolonged by admixture with oxygen; equal volumes of these two gases had a rate of 0·9008 instead of 0·72, which would be the mean of the two.

In the following table the transpirability of some vapours is given. These results, however, from the necessity of experimenting upon the bodies in a state of mixture with some permanent gas, are not equally precise with those attained in the case of the gases above enumerated:—

Transpirability of Vapours.

(Times required for equal volumes.)

Oxygen	1·0000	Ethyl Chloride	0·4988
Bromine (about)	1·0000	Methyl Oxide	0·4826
Sulphuric Anhydride ...	1·0000	Hydrocyanic Acid	0·4600
Carbonic Disulphide ...	0·6195	Ether (about)	0·4400
Methyl Chloride	0·5475		

Some very simple relations in the transpirability of several of the foregoing gases may be observed. Thus it has been found—

1. That equal *weights* of oxygen, nitrogen, air, and carbonic oxide are transpired in equal times.

2. That the velocities of nitrogen, nitric oxide, and carbonic oxide are equal.

3. That the velocities of hydrochloric acid, carbonic anhydride, and nitrous oxide are equal.

4. That the velocity of hydrogen is double that of nitrogen, of carbonic oxide, and of nitric oxide.

5. That the velocities of chlorine and oxygen are as 3 : 2.

6. That the velocities of hydrogen and marsh gas are as 5 : 4.

7. That olefiant gas, cyanogen, and ammonia have each nearly double the velocity of oxygen.

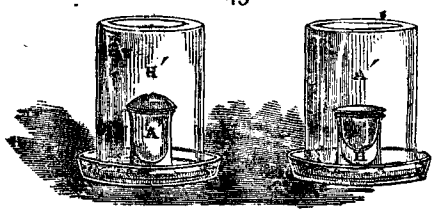
8. That the transpiration time of hydrogen is the same as that of the vapour of ether, and that of sulphuretted hydrogen is the same as the transpiration-time of the vapour of carbonic disulphide.

Carbonic oxide and nitrogen have the same density and the same rate of transpiration; so have carbonic anhydride and nitrous oxide. The rates of transpiration of atmospheric air, oxygen, nitrogen, and carbonic oxide are likewise in direct proportion to their densities; but these seem to be concurrences rather than necessary consequences, as no regular connexion between the transpiration-time and the density of the gas can be traced.

(70) *Passage of Gases through Diaphragms.*—As in the case of the diffusion of liquids the results are often modified by the employment of a diaphragm, and the introduction of the disturbing force of adhesion to the material of which it consists, so it is also in respect to gases. This disturbance of the law of diffusion is strikingly seen in the case of soluble gases, when the diaphragm is moist. If a moist thin bladder, or a rabbit's stomach, be distended with air, and suspended in a jar of gaseous carbonic anhydride, the gas being soluble in the water with which the

membrane is wetted, is conveyed through its pores by adhesion, and passes rapidly into the inside: the air in the interior is but sparingly soluble, and is transmitted outwards very slowly; the carbonic anhydride, consequently, notwithstanding its lower diffusive power, accumulates within, and at length often bursts the bladder. A similar phenomenon, arising from the same cause, is exhibited on placing a jar of air, the mouth of which is covered by a film of soapy water, in a vessel of nitrous oxide. Where the diaphragm does not exert this solvent power, the usual law of diffusiveness prevails.

FIG. 43.



This is strikingly exemplified by taking two similar small jars, shown at A and H, fig. 43, H being filled with hydrogen, A with air, and tying a sheet of caoutchouc over the open mouth of each. Over the one containing air invert a large jar full of hydrogen, H′; leave the other exposed in a jar of air A′; in the course of ten days or a fortnight the caoutchouc over the jar filled with air will have become convex from the endosmosis of the hydrogen; over the other it will have become concave from its exosmosis; the motion of the hydrogen in both cases through the caoutchouc being more rapid than the simultaneous passage of the air through it in the opposite direction.

It was proved many years ago by Mitchell, that caoutchouc has, like charcoal, the power of condensing large quantities of many gases by the force of adhesion; for example, it rapidly absorbs ammonia, nitrous oxide, and sulphurous anhydride. Indeed, it is impossible to employ any diaphragm in which this disturbing force is not in a certain degree observable; even with plaster of Paris it is appreciable, and slightly modifies the experimental results of diffusion:* where condensation occurs in the membrane to a large amount, the gas is frequently reduced in bulk as much as would be needed for its liquefaction; it then evaporates from the opposite surface of the diaphragm into the other gas, just as a very volatile liquid would do.

This action of colloids upon gases has been made the subject of careful investigation by Graham (*Phil. Trans.* 1866, 399), who regards the absorption of

* Bunsen, in his experiments (*Gasometry*, translation by Roscoe, 198-233), used a plug of gypsum from 12 to 25$^{mm.}$, or half an inch to an inch in thickness, and the results showed that the phenomena of transpiration must also be allowed for, but from estimating its importance unduly, he was led to question the accuracy of Graham's law of effusion, which is no doubt correct. An elaborate re-investigation of the whole subject by Graham has placed this beyond question (*Phil. Trans.* 1863, 385).

gases, under these circumstances, as due to a species of solution. He says (p. 403), referring to the action of rubber on carbonic anhydride, 'The first absorption of the gas by rubber must depend upon a kind of chemical affinity subsisting between the material of the gas and substance of rubber, analogous to that attraction which is admitted to exist between a soluble body and its solvent, conducing to solution. Carbonic acid being soluble in ether and volatile oils, it is not wonderful that it is also dissolved by the hydrocarbons of rubber. The rubber being *wetted through* by the liquefied gas, the latter comes to evaporate into the vacuum, and reappears on the other side of the membrane.'

In a series of experiments made upon the absorptive power of rubber upon different gases, Graham employed a diffusion tube about $22^{mm.}$ in diameter, and a metre in length, closed at the upper end by a thin plate of stucco, and open below. A thin film of rubber from a small caoutchouc balloon was stretched over the plate of stucco, secured with copper wire, and cemented to the glass with gutta percha softened by heat. The tube was filled with mercury, and inverted in a vessel of mercury so as to obtain a Torricellian vacuum, into which different gases were allowed to penetrate, by enclosing the upper end of the tube in a hood of thick vulcanized rubber, provided with an entrance and exit tube for gas. The gas to be operated on was then transmitted steadily through the chamber formed above the film of rubber by the hood; the excess of gas being allowed to escape into the air. The mercurial column gradually fell in the diffusion tube, and the time occupied during a fall of $25^{mm.}$ was observed.

Taking the time occupied for the passage through the film of a constant volume of carbonic anhydride as 1, the time occupied by the entrance of equal volumes of the following gases was found by Graham to be represented by the numbers subjoined:—

Carbonic anhydride	1
Hydrogen	2·470
Oxygen	5·316
Marsh gas (CH_4)	6·326
Atmospheric air	11·850
Carbonic oxide	12·203
Nitrogen	13·585

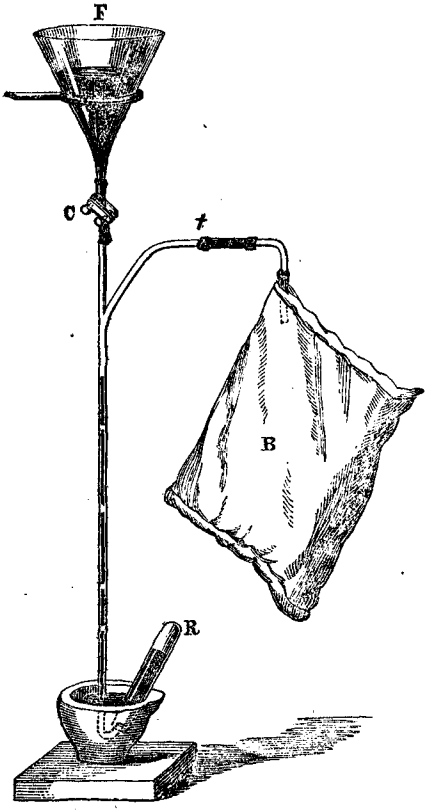
No relation between either the diffusibility of a gas or its solubility in water is exhibited by these numbers.

The penetration of rubber by gases is much affected by temperature, the softening of the film by heat increasing the rate at which permeation takes place, notwithstanding the increase of volume conferred upon the various gases by rise of temperature. Air, for instance, passed through a septum of rubber at 4° C. with only $\frac{1}{11}$ of the velocity with which it passed through the same septum at 60° C.

The difference in the facility with which oxygen and nitrogen pass through caoutchouc suggested the possibility of mechanically separating the constituents of atmospheric air to a considerable extent; and the method by which Graham was enabled to accomplish this object most readily and completely was the following:—A Sprengel's air-pump (*Chem. Soc. Journ.* 1865 [2], iii. 9) is attached by means of the branch tube, *t*, to an air-tight gas-bag, B. This bag is best made of a thin but close silk fabric, coated with black rubber upon one side only. The varnished side is turned inwards, and between the two surfaces a double thickness of common felt carpet is placed. A glass quill tube projects inwards for a few inches, and is connected by means of black vulcanized tubing, secured with coils of thin copper wire, and varnished with fused rubber. An exhausting syringe connected with the tube, *e*, is used to commence the removal of the air,

the tube being closed above by the clamp at *c*; the syringe is removed, and the funnel, F, is filled with mercury, and on relaxing the clamp, the residual air in B gains access to the descending tube, and is swept on by the falling mercury. It may be collected when desired by placing a small receiver, R, over the recurved extremity of the descending tube, which should be of $2{\cdot}5^{mm.}$ internal diameter ($\frac{1}{10}$ inch). After all the contents of the bag had been thus extracted, and the collapse was complete, the Sprengel tube began to throw out air in a slow but very regular manner. The air thus collected was found to have experienced what is regarded by Graham as a process of dialysis. A square metre of such silk (at 20° C.) allowed the passage of about 2·25 cub. centim. air per minute, and the proportion of oxygen was usually from 41 to 42 per cent. If a glowing chip be introduced into such air, it is rekindled. In one observation, at a temperature of 4° C., the proportion of oxygen in the dialysed air was found to rise as high as 47·4 per cent.

Fig. 64.



No doubt, if on a large scale it were possible by such mechanical means to reduce the proportion of nitrogen to one-half of that which exists in air, the concentrated oxygen mixture might be applied to many useful purposes.

(70 *a*) *Passage of Gases through Metallic Septa.*—Something analogous to this action of caoutchouc has been proved by the experiments of Deville and Troost to occur in the case of certain metals—viz., platinum and iron, which they found to become permeable to hydrogen at elevated temperatures in a very remarkable and unexpected manner:—A tube of hammered platinum was fitted by means of corks into the axis of a shorter and wider porcelain tube; a slow current of pure and dry hydrogen was directed through the outer tube, whilst a current of dry air was transmitted through the platinum tube. At ordinary temperatures no moisture was observed in the air which passed through the platinum tube; the porcelain tube and the platinum within were then gradually raised to a red heat; at a temperature of 1100° C. (2012° F.) the oxygen contained in the air had entirely

disappeared, nothing but nitrogen and steam passing out of the platinum tube; whilst at still higher temperatures the moist nitrogen was mixed with hydrogen. As the tube cooled, the same phenomena were observed, but in the inverse order, till at ordinary temperatures no diffusion of hydrogen was perceptible. A cast tube of platinum $2^{mm.}$ thick gave similar results. (*Comptes Rendus*, 1863, lvi. 977, and *Phil. Mag.* 1863 [4], xxvi. 336.) Carbonic anhydride does not experience diffusion in the platinum tube.

Analogous experiments upon a tube of soft cast steel drawn down to a tube the sides of which were from 3 to $4^{mm.}$ thick, showed that this material also is porous at high temperatures. In this experiment the steel tube was soldered at each end by means of silver solder to narrow tubes of copper; it was then enclosed in a porcelain tube, to protect it from the fire, and raised gradually to a strong red heat: one end of the copper tubing was connected with an apparatus which disengaged hydrogen; the other terminated in a long glass tube, which was plunged into mercury. After the hydrogen had been transmitted for several hours through the ignited tube, the tube which conveyed the gas was sealed by fusion; and immediately the mercury rose in the glass tube to a height of $740^{mm.}$ (29·13 inches), so that an almost perfect vacuum was produced by the escape of the hydrogen through the substance of the hot steel tube (*Comptes Rendus*, 1863, lvii. 965).

This subject has been pursued by Graham in the paper already quoted (*Phil. Trans.* 1866):—By means of the Sprengel pump attached to one of Deville's tubes, the platinum tube was found to be tight to either atmospheric air or hydrogen at ordinary temperatures, and at all temperatures below a dull red heat; but as soon as the outer porcelain tube became visibly red, the hydrogen passed through the pores of the platinum, and in 7 minutes, 15·47 cub. centim. of gas were collected, of which $15{\cdot}27^{c.c.}$ were hydrogen. The platinum tube which was used in this experiment was joined without solder; it was drawn from a mass of the fused metal, and was 1·1 millimetre in thickness. 1 sq. metre of such a tube delivered hydrogen, at a temperature approaching a white heat, in quantity of 489·2 cub. centim. per minute: this was nearly 4 times as fast as the passage of hydrogen at 20° C. through a septum of rubber $0{\cdot}014^{mm.}$ thick. Oxygen and nitrogen were tried under similar circumstances, but neither of these gases permeated the platinum. Carbonic anhydride, chlorine, hydrochloric acid, and aqueous vapour were equally unable to penetrate the ignited metal.

No hydrogen was found when either of the gases last named was used; therefore it may be inferred that no dissociation of their constituents occurred at this temperature. When either ammonia, coal gas, or hydrosulphuric acid was tried, pure hydrogen was found to have penetrated the tube, but none of the undecomposed gas itself passed through.

The experiments were then varied in the following manner:—A porcelain tube was fitted with quill glass tubes and sound corks, and either closed hermeti-

cally, or, when necessary, connected with a gas delivering apparatus at one extremity, and at the other with a Sprengel tube. A quantity of clean platinum wire drawn from fused metal was introduced into the porcelain tube, exhausted, and heated for an hour. Then pure and dry hydrogen was admitted into the porcelain tube at a cherry-red heat, and the temperature allowed to fall gradually, so as to expose the metal for about twenty minutes at a heat a little below redness to an atmosphere of hydrogen. It was then allowed to cool completely, and the excess of hydrogen was swept out by a current of air or of nitrogen. The closed tube was now exhausted in the cold, but no hydrogen came off. The platinum being still retained in a good vacuum, heat was again very gradually applied, and the action of the Sprengel pump maintained. Gas began to come off as soon as visible redness was attained; and in the course of one hour 201 grms. of platinum gave off $2{\cdot}12^{c.c.}$ of gas, 1·93 of which consisted of hydrogen, and 0·19 of nitrogen. The platinum had consequently absorbed one-fifth of its bulk of hydrogen (or nearly half its bulk, if calculated at a red heat) without any sensible change in lustre, or otherwise. Repeated heatings somewhat diminished the volume of hydrogen absorbed by this mass of platinum. Spongy platinum, when similarly treated, absorbed 1·48 its volume of hydrogen, with a sensible amount also of nitrogen. Sheet platinum from an old crucible absorbed a still larger quantity of hydrogen, the amount exceeding five volumes. The gas thus absorbed appears to be permanently retained. In one experiment a piece of platinum which had been charged with hydrogen was hermetically sealed in a tube with air, and left for two months. No hydrogen escaped into the tube; and on heating the platinum in the manner already described, it gave off, in different experiments, from 2·28 to 3·79 times its bulk of hydrogen. Platinum foil was observed, when heated in hydrogen only to 230° C. for three hours, to absorb 1·45 its volume of hydrogen, which could not be extracted *in vacuo* until the temperature was raised to redness. Copper, by similar modes of experiment, was found to absorb from 0·3 to 0·6 of its bulk of hydrogen, Gold absorbed 0·48 its volume of hydrogen, and 0·3 of carbonic oxide. It also absorbed nitrogen from the air to the extent of about 0·4 of its volume; 86·3 per cent. of the absorbed gas consisting of nitrogen, 5·3 of oxygen, and the remainder 8·4, of carbonic anhydride. Silver wire absorbed 0·21 its volume of hydrogen, and 0·745 of oxygen. In three different experiments silver sponge (reduced from the oxide) retained 6·15, 8·05, and 7·47 volumes of oxygen, at all temperatures below incipient redness, but showed no visible tarnish of its surface.

Iron wire retained from 0·46 to 0·42 its volume of hydrogen. The same iron, after the expulsion of the hydrogen, was exposed to carbonic oxide: the pure iron was thus found to be capable of taking up at a low red heat, and holding when cold, 4·15 volumes of carbonic oxide. The wire remained soft, and did not become hard when heated red hot and suddenly cooled, neither was it altered in aspect or in solubility in acids. Indeed, as Graham remarks, 'in the course of its preparation wrought iron may be supposed to *occlude* six or eight times its volume of carbonic oxide gas, which is carried about ever after.' This diffusion of carbonic oxide through the mass of the iron is regarded by Graham as the ordinary means of distributing carbon through iron in the process of converting it into steel. The Lenarto meteorite was found to contain 2·85 times its volume of gas, of which 85·68 per cent. was hydrogen, 9·86 nitrogen, and 4·46 carbonic oxide (*Proc. Roy. Soc.* 1867, xv. 502).

The most remarkable results upon the absorption of gases by the metals were obtained in the case of palladium. A particular piece of palladium foil was first heated *in vacuo* to redness, and then exposed, at a heat not exceeding 245° C., to hydrogen, after which it was allowed to cool very slowly. When exposed at ordinary temperatures *in vacuo*, it gave off no hydrogen; but as soon as heat

was applied, the gas was evolved freely, and amounted to 5·26 volumes for 1 volume of the metal. The same piece of foil, when heated for three hours to between 90° and 97° C., absorbed 643·3 volumes of hydrogen; and if the metal, after heating to redness, was allowed to cool *in vacuo*, it absorbed, even at common temperatures, fully 376 volumes of the gas. No alteration was sensible in the metallic appearance of the foil. Spongy palladium took up 686 volumes of hydrogen, but exhibited no tendency to absorb oxygen or nitrogen. Palladium foil prepared from a piece of the metal which had been fused, absorbed hydrogen much less abundantly; the maximum amount not exceeding 68 volumes.

A still larger quantity of hydrogen can be occluded by palladium when a wire of this metal is made the negative pole of a voltaic cell, decomposing water acidulated with sulphuric acid. As much as 936 volumes of hydrogen may thus be absorbed by 1 volume of palladium. During this occlusion, the palladium increases in bulk in the proportion of 100 to 104·908, or sixteen times the expansion it would undergo in being heated from 0° to 100° C. On heating the metal charged with hydrogen *in vacuo* the gas escapes, and the metal contracts to an extent nearly double of that which it had expanded in absorbing the hydrogen: thus a wire of palladium $609{\cdot}144^{mm.}$ long expanded, on absorbing 936 volumes of hydrogen, to a length of 618·923, showing an increase of 9·77; after heating *in vacuo* the length was found to be $599{\cdot}444^{mm.}$, or a contraction from the original length of 9·7. This contraction is in length only, for the density of the palladium at the conclusion of the experiment is almost exactly what it was at the commencement.

On making a piece of palladium charged with hydrogen the positive pole of the battery, the hydrogen is rapidly converted into water by the nascent oxygen; and by proper arrangements the expansion and contraction of the metal can easily be observed on reversing the current in the cell.

Palladium charged with hydrogen is liable to become suddenly hot when exposed to the atmosphere, and the hydrogen removed by oxidation; on heating the end of a piece of charged wire by a spirit-lamp, the hydrogen burns, and the flame travels along the wire.

From the measurements of the expansion and contraction of palladium on absorbing and losing hydrogen, Graham has calculated that the density of hydrogen in this condition (or *hydrogenium*, as he has named it) is between 0·854 and 0·872.

The metal when charged with hydrogen, perfectly retains its metallic lustre, and will even receive an impression in a coining press without alteration.

A solid palladium tube $1^{mm.}$ thick was found to be tight to atmospheric air when heated to redness; but at a temperature of 240° C., hydrogen began to pass through it; and when it was heated to a point just short of redness, the gas passed at the rate of 423 cub. centims. per minute for a square metre of surface.

When coal gas was employed instead of pure hydrogen, and the heat was raised to 270°, pure hydrogen, completely free from any smell of coal gas, passed into the interior of the metallic tube. Ether vapour was found to pass through palladium foil at common temperatures, although hydrogen did not pass.

From these remarkable investigations Graham concluded that there is a progression in degrees of porosity. He says, 'there appear to be (1) pores through which gases pass under pressure, or by capillary transpiration, as in dry wood and many minerals; (2) pores through which the gases do not pass under pressure, but pass by their proper molecular movement of diffusion, as in artificial graphite; and (3) pores through which gases pass neither

by capillary transpiration, nor by their proper diffusive movement, but only after liquefaction—such as the pores of wrought metals and the finest pores of graphite.'

This latter porosity Deville conceives to be an *intermolecular* porosity due entirely to dilatation. The intermolecular porosity of platinum and iron is not sufficient, he supposes, to admit any passage of gas at low temperatures, but is developed by the expansive agency of heat upon these metals, and becomes sensible in these particular cases about the temperature of ignition.

The absorption of a gas by a liquid or a colloid substance is not a purely physical effect. Some relation in composition is necessary; hence it is asked by Graham whether a similar analogy may not be looked for between hydrogen and colloid bodies of the metallic class.

The phenomena of diffusion in gases were viewed by Dalton as a necessary consequence of the self-repulsive property of the particles of gaseous bodies. He considered that each gas ultimately dilates until the whole space through which the diffusion occurs is filled with an atmosphere of that gas, of a density proportional to the quantity of the gas present. Observation shows that each gas becomes diffused through a limited space filled with any other gas, as it would be through a vacuum, the other gas only acting mechanically to retard the period at which such uniformity of diffusion is attained.

It has been remarked by Graham, that if this view were true, there should be, contrary to experience, a depression of temperature when two gases become intermixed. It does not, however, appear that this is a necessary consequence, since the particles of each gas may merely glide amongst those of the other kind, as the particles of water do amongst those of sand, the self-repulsion of the particles still being the power which determines the process of diffusion.

The phenomena of the diffusion of liquids seem, however, to be more easily reconciled with the supposition of a feeble superficial attraction between the particles of one liquid and those of another, and the supposition that an analogous attraction exists between the particles of one gas and those of a gas of different nature might sufficiently account for the process of intermixture in the case of elastic fluids.

It is to be borne in mind that in the intermixture of gases, the diffusion volume has no necessary relation to the chemical equivalent of the body. The ratios which have been observed are dependent upon the relative density of the gases compared,

quite irrespective of the combining proportion. In liquids, a similar want of connexion between the chemical equivalent and the diffusion volume is observed; the relation in this case is a multiple of the absolute weight diffused.

(71) *Separation of Bodies by Cold or Heat.*—It often happens, where adhesion has proceeded so far as to produce the solution of a solid in a liquid, as in the cases just considered, that the chemist has occasion to destroy this adhesion, and to obtain one substance or both of them in a separate form. This separation is generally effected with the aid of heat. Depression of temperature will sometimes cause the cohesion of the particles of the solid to acquire the ascendancy over the force of adhesion. When, for example, brandy is exposed to intense cold, many degrees below that necessary to freeze water, the spirituous portion retains its liquid form, and separates from the aqueous part, which solidifies as ice. Indeed water, in the act of freezing, becomes completely separated from everything which is previously held in solution. It is owing to the separation of air previously dissolved in the water, that ice so often presents a blebby, honeycombed appearance.

Faraday has shown that, even on a small scale, this complete separation of foreign matters from water may be easily effected by the process of freezing:—If sulphuric acid, or a strong solution of indigo, or one of common salt, be mixed with 90 or 100 times its volume of water, and this mixture be placed in a tube of about an inch in diameter, and immersed in a freezing mixture (175), at the same time that the separation of the foreign matter is mechanically facilitated by stirring the liquid round and round briskly and constantly with a feather, the sides of the tube will, in a few minutes, be lined with a coat of transparent, chemically pure ice, all the foreign matters having accumulated in the central portion, which still remains liquid.

It would appear that when the freezing of saline solutions takes place on a large scale, as in the neighbourhood of the Poles, the ice formed is by no means free from salt. Mr. Walker, who accompanied Sir L. M'Clintock in the *Fox*, made numerous observations on the freezing of sea water in the Arctic regions. He found that when the temperature fell below $-2°$ C., ice began to form, at first as a thin pellicle, which gradually acquired a vertically striated appearance as it increased in thickness, plumose saline crystals separating upon the surface of the ice. Although he observed the formation of ice from sea water at all temperatures between $-2°$ and $-41°$ C., he never from this source could

obtain ice which on melting furnished fresh water. The purest ice was that formed at the lowest temperature; but even that when melted furnished water of sp. gr. 1·005. He re-melted the ice from sea-water, and froze it again, repeating the operation several times upon the same portion of water, but never by this means succeeded in obtaining water of less density than 1·002. Dr. Rae found that the ice of the previous winter, if above the level of the surrounding water, was usually fresh, probably from the draining away of the unsolidified brine previously entangled in the ice. (*Proc. Phys. Soc.* 1874, i. 14.) Mr. Buchanan made some experiments during the Antarctic cruise of the *Challenger*. He found that when pack ice was melted, the liquid which first flowed away contained more salt than the later portions, and that before the whole of the ice has disappeared, its temperature had risen from -1° to 0° C. At this temperature almost fresh water was obtained. (*Proc. Roy. Soc.* 1876, xxiv. 609.) Dr. Guthrie has shown that when sea-water is frozen on a small scale by a freezing mixture, and the ice immediately strongly pressed between flannel, the ice contains only $\frac{1}{13}$ of the quantity of salts present in the original water. (*Proc. Phys. Soc.* 1874, i. 72.)

In studying the effect of cold on solutions, Dr. Guthrie (*Proc. Phys. Soc.* 1874, i. 53, 1875, ii. 1 and 53) has obtained some very remarkable results. The first series of experiments was conducted on solutions of sodic chloride in water. When a dilute solution of this salt is cooled below 0° C. with constant stirring, ice is gradually deposited, the temperature at which the ice forms depending on the quantity of salt present. Thus a solution with 5·254 per cent. of salt deposits ice at $-3^{\circ}\cdot4$, with 10·508 per cent. at $7^{\circ}\cdot7$, with 15·762 per cent. at $-12^{\circ}\cdot4$, and with 18·389 per cent. at $-15^{\circ}\cdot4$. If, on the other hand, a saturated brine containing 26·27 per cent. of salt is cooled, a different result is observed; at -7° crystals of the hydrate of sodic chloride NaCl, $2H_2O$ are deposited, and this continues until the temperature reaches -22°, when the whole solidifies. By separating the crystals as they are formed until the temperature falls to -22°, a liquid is obtained possessing a composition approximately represented by the formula $2NaCl,21H_2O$, and which solidifies at -22°, the solid exhibiting a constant fusing point. This compound, or *cryohydrate*, may be, therefore, produced on cooling either a dilute solution, when ice first separates; or a strong solution, when salt first separates. The same treatment has been applied to a large number of other solutions with perfectly similar results, a series of cryohydrates being formed, each possessing a

definite fusing point and composition. The fusing point of the cryohydrate is the minimum temperature obtainable by a freezing mixture of the salt and ice. In the case of salts which are more soluble in hot water than in cold, the curve indicating the solubility of the salt in water above 0° is continuous with that representing the temperature at which the salt is deposited by cooling the solution below 0°; it continues regular until the fusing point of the cryohydrate is reached, when it returns abruptly towards 0°.

In like manner, gases may be in a great measure freed from condensible vapours by exposing them to a very low temperature. Air saturated with moisture may be rendered nearly dry by causing it to traverse a long tube, cooled down by immersion in a mixture of ice and salt.

Elevation of temperature is still more often resorted to for the separation of bodies in solution: when, for instance, a solution of common salt in water is exposed to heat, the repulsive power of this agent overcomes the cohesion of the water, as well as its adhesion to the salt; the water assumes the aëriform condition, passes off in steam, and leaves the salt behind in the solid state. This process is termed *evaporation*. It proceeds rapidly in shallow, open vessels, in which case the liquid escapes into the air. If it be necessary to preserve the solvent, the operation is conducted in a closed vessel, such as a retort, and connected with a suitable condensing apparatus, so as to effect a *distillation* of the liquid. The same process may be applied to effect a partial separation of liquids of different degrees of volatility; and spirit of wine is thus more or less perfectly separated from water.

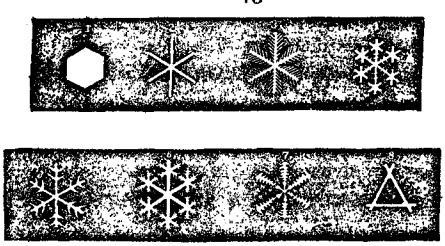
§ IV. Crystallization.

(72) *Modes of procuring Crystals.*—It might be anticipated that when cohesion slowly recovers its ascendancy, this force would exert itself throughout the mass equally in all directions, and that a globular concretion would be the result, as when oil separates from mixture with dilute spirit of a specific gravity precisely equal to its own. The fact, however, is quite otherwise, for as a general rule cohesion is not exerted equally in all directions in solids. In the majority of instances, where solid bodies are allowed to separate slowly from their solutions, they are found to assume regular geometrical forms. Each substance has its own peculiar form. Such regular geometrical solids are termed *crystals*.

By these differences in form, the materials which constitute the crystallized masses may often be distinguished from each other. For example, common salt crystallizes in cubes, alum in octohedra, saltpetre or nitre in six-sided prisms, Epsom salts in four-sided prisms, and so on. The more slowly and regularly the process is allowed to proceed, the larger and more regular are the crystals. The usual method of obtaining crystals is to form a strong solution of the salt in hot water, for most bodies are more freely soluble in water when it is at an elevated temperature than when cold; as the liquid cools, the cohesion of the salt resumes its ascendancy, and the crystals shoot through the liquid: in this way crystals of nitre are easily procured.

It is not necessary, however, that the liquefaction should in all cases take place through the intervention of an indifferent liquid such as water: mere fusion of the substance, followed by slow cooling so as to allow it freely to obey the molecular attraction, is in many instances sufficient to produce crystals. If 2 or 3 kilogrammes of sulphur or of bismuth be fused in a crucible, and, after it has cooled sufficiently to become solid upon the surface, the crust be broken through and the yet liquid sulphur or bismuth be poured out, the inner surface of the solid portion will be found to be lined with prismatic transparent crystals of sulphur, or brilliant hollow cubes of metallic bismuth. Water on solidifying often shoots into beautiful crystals, as may be seen in the forms of snow-flakes, fig. 45, which fall during a hard frost. The forms of these flakes are all derived from the six-sided plate. No. 1; the separate crystals in the groups 2, 3, 4, 5, 6, 7, 8, all cross each other at angles of 60° and 120°, though they vary in the complexity of their arrangement.

FIG. 45.



In the bowels of the earth, temperatures which man can hardly attain in his furnaces, have been acting for ages; processes of cooling of the most regular and gradual kind have been proceeding, and a great variety of combinations have been effected under the pressure of the superincumbent strata. By the combined operation of these causes many crystalline substances of mineral origin have been formed, which we have not succeeded in imitating, although a closer examination of the slags of our

iron furnaces reveals new artificial formations of this nature; and the number of those combinations, previously unattained by art, is gradually being diminished.

Ebelmen (*Ann. Chim. Phys.* 1848 [3], xxii. 211) succeeded in producing a variety of artificially crystallized compounds, which were before only known as natural minerals, by dissolving their constituents in boracic or in phosphoric acid, or in one of their salts, and then subjecting the mixture to an intense and long-sustained heat in a furnace used for baking porcelain; the acid, or other compound employed as the solvent, was thus very slowly volatilized, and various minute crystals were obtained, including spinelle, chrome iron, emerald, and corundum or ruby.* Deville and Caron (*Comptes Rendus*, 1858, xlvi. 764) have extended these experiments. They introduced the fluorides of certain metals into a crucible lined with charcoal, and containing a quantity of boracic anhydride supported in a small cup of carbon. The cover of the crucible was then carefully luted on, and the whole exposed for an hour or two to an intense white heat. Under these circumstances the metallic fluoride and the boracic anhydride were slowly volatilized, the vapours decomposed each other, and crystals were formed. Ferric fluoride when thus treated yielded magnetic oxide of iron in octohedral crystals; zirconic fluoride yielded dendritic crystals of zirconia; a mixture of aluminic and glucinic fluorides furnished chrysoberyl (GO,Al_2O_3); aluminic fluoride mixed with zincic fluoride yielded crystals of gahnite (ZnO,Al_2O_3); and, by the use of appropriate mixtures, staurolite† and other crystallized bodies previously only known as native minerals were procured. The success that has attended these investigations offers every inducement, to those who have the opportunity, to pursue this interesting subject.

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* Some recent experiments by Knop on titanic anhydride crystallized from microcosmic salt have shown that the compound thus obtained, and supposed to be anatase, is a phosphotitanic anhydride, $3\,TiO_2, P_2O_5$.

† Few transformations of this kind are more instructive than those which accompany the formation of staurolite, the crystallized silicate of alumina ($4\,Al_2O_3, 3\,SiO_2$). Alternate layers of silica and alumina are placed in a porcelain tube heated to redness, and through this a current of silicic fluoride is transmitted, and escapes apparently quite unaltered at the other end of the tube. The fluoride attacks the ignited alumina, removing oxygen from it. This oxygen combines with a portion of the silicon of the fluoride, producing silica which unites with a portion of the alumina, $3\,SiF_4 + 2Al_2O_3 = 3\,SiO_2 + 2\,Al_2F_6$. Meantime, aluminic fluoride being volatilized, passes on and attacks the superincumbent layer of ignited silica. Alumina is reproduced, and combines with a portion of the silica, whilst silicic fluoride is again formed, again to undergo a similar series of transformations, $2\,Al_2F_6 + 3\,SiO_2 = 3\,SiF_4 + 2\,Al_2O_3$.

The prolonged action of water at high temperatures, such as can only be obtained under pressure, often furnishes crystalline compounds which cannot otherwise be procured. Acting upon a knowledge of this fact, De Senarmont, by operating in closed vessels with water upon various compounds, at temperatures ranging between 266° and 572° (130° and 300° C.), succeeded in obtaining in a crystallized condition the principal minerals which occur in metalliferous veins, including quartz, carbonates of iron, manganese, and zinc, baric sulphate, antimonious sulphide, mispickel, and red silver ore, as well as anhydrous ferric oxide, and corundum. (*Ann. Chim. Phys.* 1851 [3], xxxii. 129.)

The prolonged action of water at moderate temperatures may often also, as Daubrée (*Comptes Rendus*, 1858, xlvi. 1086) has shown, cause the formation of complicated crystallized minerals. It was found by this mineralogist that the zeolites apophyllite, chabasite $[(KNaCa_{\frac{1}{2}})_2O, Al_2O_3, 4SiO_2, 6H_2O]$, and harmotome $[K_2O, 2CaO, 3Al_2O_3, 12SiO_2, 15H_2O]$, have gradually been produced in the concrete laid down by the Romans around the channels of outflow, at the hot springs of Plombières.* Tetrahedrite (grey copper) has been found at Bourbonne-les-Bains, Haute Marne, where it has been produced by the corrosion of copper coins by mineral water.

It is not in all cases necessary that liquefaction should take place as a preliminary to crystallization: a solid when deposited from the gaseous state sometimes furnishes crystals: iodine, arsenious anhydride, sulphur, mercuric iodide, and camphor, offer illustrations of this mode of crystallization. Some solids change their crystalline form entirely when left in the liquid from which they are deposited: thus benzamide when separating from its solution in boiling water forms a mass of fine needles; after a time a change takes place and solid crystals begin to grow amongst the needles, and ultimately the latter are entirely transformed into large solid transparent crystals.

(73) *Separation of Salts by Crystallization.*—The process of crystallization from solution often affords a means of separating

* This concrete rests in part on granite and in part on alluvial gravel. The mineral water flows out at a temperature ranging between 140° and 158° (60° and 70° C.). It is very dilute, containing not more than 0·3 gramme per litre of saline matters, or 21 grains per gallon. It holds in solution small quantities of silica, and salts of sodium, potassium, calcium, and aluminium. These substances thus, in almost infinitesimal quantities, penetrate the concrete by a very slow infiltration, and in the lapse of ages have altered its composition, and deposited regularly crystallized zeolitic minerals.

two salts of unequal solubility, the crystalline form of which is different, and which have no chemical action on each other: nitre is thus purified from the common salt which always occurs mixed with it. This process is very generally resorted to as a means of purifying salts from small quantities of foreign admixtures, which may be soluble in water, but which either do not crystallize, or if they crystallize, do not do so in dilute solutions. Each crystallization diminishes the quantity of adhering impurity, and after the process has been repeated three or four times, dissolving each successive crop of crystals in fresh portions of pure water, the product will in most cases be free from impurity. The crystallization of sea-salt from sea water thus separates the sodic chloride from magnesic chloride, and from various other salts which are present with it in small proportions; a single crystallization gives the salt sufficiently pure for commercial purposes, though it is in this state far from being chemically free from the bodies which accompany it in the waters of the ocean. A single crystallization of many salts, however, may be made to furnish the salt very nearly chemically pure, if the solution be briskly stirred whilst the crystals are being formed. The salt is thus deposited in minute detached grains; and if these are placed to drain, and washed with a saturated solution of the pure salt, as is practised in the refining of nitre (552), the *mother liquor*, which retains the impurities dissolved, may be completely washed away; but if the crystals be allowed to be deposited slowly and to acquire a large volume, the mother liquor is retained between the layers of each crystal, and cannot be thoroughly displaced by the pure solution. Bodies which possess the same crystalline form, such as potassic sulphate and chromate, cannot thus be separated from each other by crystallization.

(74) *Sudden Crystallization: Nuclei.*—Where the forces of cohesion and adhesion are nearly balanced, as in saturated solutions, very slight causes may occasion the cohesion to preponderate; and when once this force has been set in action, its influence spreads rapidly throughout the mass. Water, for example, in a still atmosphere, may be cooled 8 or 10 degrees below the freezing point, and yet continue liquid; but the slightest vibration of the vessel causes sudden crystallization of a portion of the liquid into ice. Sometimes a similar effect is produced, as in the case of Glauber's salt, by the sudden admission of air to the solution of the salt saturated at a high temperature, and from which the air has been expelled by boiling (55).

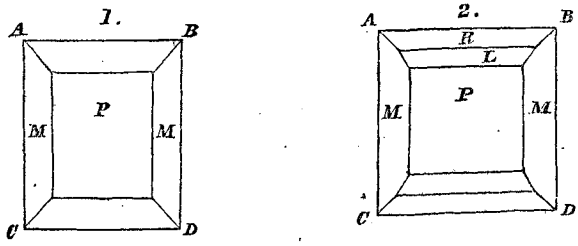
Adhesion to a solid body may be sufficient to disturb the

balance; thus, the dropping in of a similar crystal, the insertion of a thread, or of a wire, or of a piece of stick, if not sufficient to cause sudden crystallization, will generally determine the spot upon which the crystals are first formed, especially if the foreign body or nucleus be rough and irregular in its outline. For this reason threads are stretched across the vessels in which the pure solution of sugar is set aside to crystallize in the manufacture of sugar-candy; so also wooden rods are placed in solutions of cupric acetate, and copper wires are suspended in solutions of borax in order to facilitate the crystallization of the salt.

(75) *Circumstances which modify Crystalline Form.*—The volume of crystals is often influenced by circumstances apparently trivial. Muddy solutions generally yield the largest crystals, as is well seen in the manufacturing process for obtaining citric and tartaric acids, where the impure acid always forms the finest crystals. Occasionally the presence in the liquid of a substance which does not crystallize with the salt, yet modifies the form which the latter assumes; urea, for instance, occasions the deposition of common salt in octohedra instead of its usual form of the cube. Potassic iodide generally crystallizes in cubes, but under certain conditions, and especially when the solution is quite pure, prismatic crystals are produced. Sodic carbonate usually crystallizes in large transparent solid crystals, but when quite pure the crystals are platy and not at all compact. It was also found by Jacobsen (*Pogg. Annal.* 1861, cxiii. 498) that sodic chlorate, which crystallizes ordinarily in cubes, could be obtained at pleasure in the hemihedral form observed by Marbach, by touching one of the regular cubic crystals of the salt with a little fat or wax, and putting it back into the mother liquor. A similar modifying influence on the form of the crystal was produced by the addition of small quantities of urea, of glycerin, or of crude hydric potassic tartrate to the mother liquor.

The investigations of Pasteur (*Ann. Chim. Phys.* 1857 [3], xlix. 5) have thrown an interesting light upon some of the causes which thus operate in modifying the form of crystals. The crystals which were particularly examined by him were those of acid malate or bimalate of ammonium ($H_4NH\,C_4H_4O_5$), and of strontic formiate. Bimalate of ammonium, when it is deposited in the cold from a pure saturated solution of the salt, crystallizes in the form shown in No. 1, fig. 46—a form derived from a right prism with a rhombic base. Sometimes,

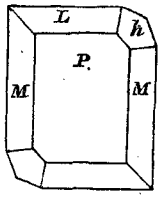
FIG. 46.



however, the crystals exhibit the double bevel shown in No. 2. When the salt is deposited from a solution containing products of the decomposition of the bimalate by heat, it assumes a hemihedral modification, similar to one or other of those shown in fig. 47. The bimalate has a ready cleavage parallel to the sides A B

and C D (fig. 46). If a crystal of the form of 1 or 2 be broken across, as in fig. 48, and be transferred to a portion of pure saturated mother liquor, the bevel

FIG. 47.



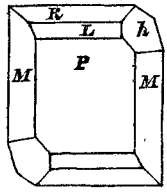
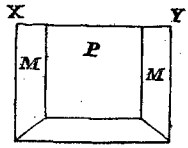
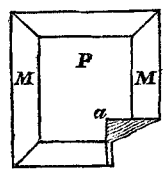


FIG. 48.



is rapidly restored: it makes its appearance first along the edges of the cleavage plane, X Y, and the growth of the crystal is more rapid in the direction perpendicular to the plane of cleavage than it is in the direction parallel with it. If the crystal be cut at one of its angles, as at *a*, fig. 49, the notch becomes rapidly filled up, and when the form of the crystal is restored, its growth again becomes regular in all directions.

FIG. 49.



The general conclusion to which these observations point is—that when a broken crystal is replaced in its mother liquor, it continues to increase in every direction; but that its growth is especially active upon the broken surfaces, in consequence of which the general outline of the figure is restored in a few hours.

If a hemihedral crystal, such as either of those shown in fig. 47, be placed in a saturated solution of the pure bimalate, the hemihedral faces quickly disappear, as the artificial injury does. On the other hand, if perfect crystals be placed in a mother liquid depositing hemihedral crystals, the hemihedral form is speedily developed upon the newly-introduced crystals, the hemihedral crystal growing most rapidly in the direction of its length, A, B, whilst the regular crystal increases most rapidly in the direction of its breadth, A, C.

In reflecting upon this last observation, it occurred to Pasteur that if he could by mechanical means compel a crystal to increase more rapidly in length than in breadth, he might compel a pure solution to deposit hemihedral crystals. He accordingly pasted stripes of tinfoil over the sides of a well-formed crystal of the bimalate, and having produced cleavage planes at the two ends parallel to A, B, he placed it in a solution of the pure salt; on the following day the bevels had reappeared along the broken faces, and each of the four solid angles of the crystal exhibited a hemihedral face. When the tinfoil was pasted along one edge only of the crystal, the hemihedral faces were developed on that side only.

(76) *Change of Volume in Crystallizing.*—Some change of volume usually occurs at the moment of solidification; in many instances expansion takes place. Ice, for example, at the moment of congelation, increases in volume about $\frac{1}{12}$, and expands so forcibly as to burst the vessel in which it is contained. Instances of this occur during severe frosts in the pipes used for conveying water. This expansive force is so enormous that no vessels have been found sufficiently strong to resist it. Major Williams (*Trans. Roy. Soc. Edin.* 1790, ii. 23) made some experiments at Quebec

in 1784 and 1785 with 12-inch iron shells, filled with water, and closed by wooden plugs, and exposed to a temperature of about $-28°$ C. ($-18{\cdot}4$ F.). In one case the shell was split by the expansion of the freezing water, and a sheet of ice projected from the crack formed in consequence of the sudden relief of the pressure (175, *note.*) In another experiment the wooden plug was thrown more than a hundred yards, and a cylinder of ice 8 inches in length protruded from the hole. The most compact ice has a density of 0·923: 1000 parts of water at 0° C. become dilated on freezing to about 1083.* It is owing to the expansion which occurs at the moment of solidification in iron and in Newton's fusible metal, that they answer so admirably for castings. Other solids, however, present equally remarkable instances of contraction, of which mercury, lead, and gold are illustrations, and hence the unfitness of the two metals last mentioned for the purposes of casting or moulding.

According to the experiments of Kopp (*Liebig's Annal.* 1855, xciii. 129), all the under-mentioned substances contract on solidifying, and their expansion at the moment of fusion is the following:—

100 Parts of Solid	expand	on melting at	
		° F.	° C.
Phosphorus	3·43	111·2	44
White Wax	0·423	147·2	64
Stearic Acid	11·0	158	70
Sulphur	5·0	239	115

Many solids expand with much greater rapidity near their melting point than at lower temperatures; this is particularly remarkable in the case of wax. Kopp also finds that many hydrated salts expand at the moment of fusion, as for example:—

100 Parts of Solid	expand	on fusing at	
		° F.	° C.
Calcic Chloride ($CaCl_2$, 6 H_2O)	9·6	84·2	29
Hydric Disodic Phosphate (Na_2HPO_4, 12 H_2O) ...	5·1	95	35
Sodic Thiosulphate (Hyposulphite) ($Na_2S_2O_3$, 5 H_2O)	5·1	113	45

A similar phenomenon attends the melting of Rose's fusible metal (2 parts of bismuth, 1 part of tin, and 1 of lead), which on liquefying, between 203° and 209° (95° and 98° C.), expands

* Dufour found, as the result of 22 careful experiments, that the density of ice varied between 0·914 and 0·923, with a mean of 0·917: Bunsen's recent experiments, conducted with great precautions, lead to the number 0·91674 for the density of ice at 0° (*Pogg. Ann.* 1870, cxli. 1).

1·55 per cent. Iodine, bromine, potassium, sodium, tin, and bismuth, also contract at the moment of solidification, and of course expand on liquefaction.

(77) *Dissection of Crystalline Masses.*—An interesting proof of the influence of mass upon cohesion is sometimes observed in the gradual conversion of small crystals left in the liquid into larger ones. In nickelous sulphate, for example, slight alternate elevations and depressions of temperature cause the alternate solution and recrystallization of part of the salt; the smaller crystals, which offer the largest surface in proportion to their mass, are most readily dissolved, and their solution crystallizes again upon the surface of the larger ones, which thus increase in size gradually, whilst the smaller ones entirely disappear. Sparingly soluble compounds, by prolonged digestion in an appropriate solution, may sometimes be obtained in crystals. Amorphous argentic chloride may be thus gradually converted into crystals if digested in weak hydrochloric acid in sealed tubes. Many naturally crystallized minerals have doubtless increased in bulk considerably since their first deposition by this continuous process of alternate solution and crystallization.

By the slow action of solution, crystalline structure may often be made visible where no trace of it was previously apparent, and a kind of dissection of the mass is thus effected, owing to the more powerful exertion of cohesion in certain directions; these directions vary with the particular crystalline form of the compound. These phenomena may be developed in a striking manner upon the surface of a sheet of tin plate, by gently warming the plate, and washing it over while hot with a little weak acid; the crystalline forms thus displayed constitute, when the surface has been varnished, the ornamented tin plate termed *moirée métallique*. A bar of nickel placed in dilute nitric acid becomes covered with tetrahedra, from the solution of the intervening uncrystallized portions of the metal; and the fibrous structure of the better kinds of iron may be strikingly exhibited by a similar treatment of the mass. In all these cases the action of the solvent must be very weak, otherwise the force of adhesion will act too uniformly: the more slowly the solution takes place, the more clearly is this difference in the amount of cohesion in different directions of the solid manifested. Salts may be made to show the same kind of structure without having recourse to chemical solvents. A shapeless block of alum, when placed in a nearly saturated solution of the salt, becomes gradually embossed with portions of octohedra, so that its true crystalline structure is revealed to the eye. (Daniell, *Quart. Journ. of Science*, 1816, i. 24, and *Roy. Inst. Journ.* i. 1.) Tyndall has studied the dissection of ice, by which its crystalline structure is exhibited (175).

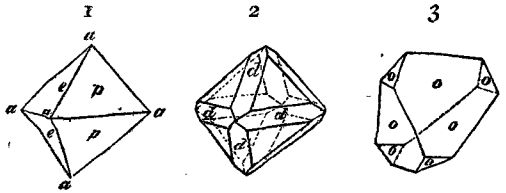
A remarkable molecular change sometimes takes place in bodies without their undergoing any alteration from the solid to the liquid state. Both brass and silver, for example, when first cast or wrought, possess considerable toughness, and neither of them has any apparent crystalline structure; by repeated heatings and coolings, however, they often become so brittle as to snap off upon the application of a very slight degree of force, and the surface of the fracture then exhibits a distinctly crystallized appearance. In the same way it is found that constant vibration, such as that to which the iron shafts of machinery and the axles of railway carriages are subjected, gradually destroys the fibrous character to which the iron is chiefly indebted for its toughness, and renders it crystalline and brittle. A similar change sometimes occurs in crystallized bodies: in this way transparent prismatic crystals of nickel sulphate or of zinc seleniate, when exposed for a few minutes to the sun's rays, become opaque; they retain their form until touched, and then crumble down into a granular powder composed of octohedral particles. An alteration somewhat similar occurs in barley sugar,

which, when first made from melted sugar, is vitreous and transparent; but it gradually becomes crystalline, opaque, and brittle.

(78) *Structure of Crystals: Cleavage.*—By the careful application of mechanical force, crystalline form may be often revealed in a body which at first appears as a shapeless mass. If to an irregular fragment of Iceland spar, for example, we apply the edge of a knife, and tap it gently on the back with a hammer, we shall find that in certain positions the spar splits readily, leaving smooth surfaces, and that having once obtained such a surface, we may go on splitting the mineral in layers parallel to the surface. Upon applying the knife to the surface of a layer so detached, we find that this layer admits of cleavage in two directions, so that ultimately a rhombohedral crystal is obtained from the spar. Some bodies admit of cleavage with much greater facility than others; and very often cleavage occurs more readily in the direction of one of the planes than in that of the others. Selenite, one of the forms of calcic sulphate, has three cleavages, but one of these is much more easily effected than the others; hence the mineral is readily split into laminæ.

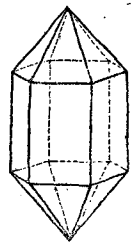
Crystals are bounded by flat surfaces termed the *faces* or *planes* of the crystal (such as *p p*, fig. 50, 1). The lines, *e e*, formed by the junction of two of these planes are its *edges;* the junction of two edges forms a *plane angle;* and the point, *a*, at which three or more planes meet, constitutes a *solid angle.* These *planes* are said to be *similar*, when their corresponding edges are proportional, and their corresponding angles equal. *Edges* are *similar*, when they are produced by the meeting of planes respectively similar, at equal angles; and *angles* are *similar*, when they are equal, and are contained within edges respectively similar. Sometimes it happens that the crystal is bounded in all directions by perfectly equal and similar faces, as is seen in the cube, the octohedron, and the rhombohedron. Such forms are distinguished as *simple forms;* whilst those forms resulting from the combination of two or more simple ones are termed *compound* or *secondary forms.* A crystal of quartz, consisting of a six-sided prism, terminated by two six-sided pyramids (fig. 51), is a compound form. In fig. 50, 2 is a compound form,

FIG. 50.



the twelve edges of the octohedron, *d d d*, being replaced by faces of the rhombic dodecahedron.

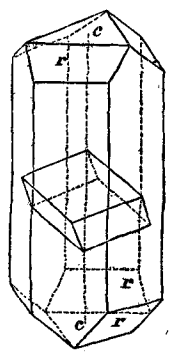
Fig. 51.



Although each substance has its own peculiar crystalline form, as, for example, alum the octohedron, common salt the cube, calcic carbonate the rhombohedron, it frequently happens that the regularity of the crystalline form is interfered with. Extra faces are often formed by the *replacement* of an edge, or the *truncation* of an angle. If the twelve solid edges of the octohedron were removed, a form intermediate between the octohedron and the rhombic dodecahedron would be the result, such as is seen in fig. 59, 2. If the four solid angles of the tetrahedron were removed, a form intermediate between the tetrahedron and the octohedron would be obtained (fig. 50, 3).

In the discovery of the simple form of crystals, the process of cleavage just alluded to is most valuable; and by its means, secondary forms, which at first sight present no resemblance to the original, may be readily traced to it. A striking instance of this kind is afforded by the cleavage of the six-sided prism of calcareous spar. By cleavage, the three alternate edges of the base may be removed, and three faces produced, as at *r r*, fig. 52, whilst a cleavage similar to that of the base may be effected upon the opposite extremity of the prism, except that the edges corresponding to those that before resisted, now yield, and that those which at the base yielded to cleavage now remain entire. The obtuse rhombohedron is thus obtained by pursuing the dissection, as shown in fig. 52.

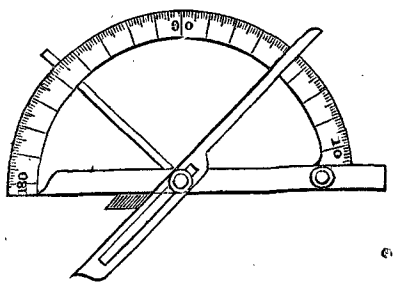
Fig. 52.



(79) *Goniometers.*—Since the number of geometrical solids is limited, whilst the number of crystallized bodies is very great, it necessarily happens that several different substances possess the same crystalline form, and the only difference observable between them consists in the different inclination of the planes to each other; or, what is the same thing, in variations of the angles of the crystal. In order to detect this difference, the crystallographer requires instruments for measuring these angles. Such instruments are termed *goniometers* (from γωνία, an angle). Of these the simplest consists of a pair of double compasses, the pivot of which coincides with the centre of a graduated semicircle; one limb is fixed, forming the diameter of the semicircle, the other is movable on the pivot, and crosses the fixed limb at its

centre, as shown in fig. 53. The external limbs of the compasses are pressed against the two planes of the crystal, the inclination of which is to be measured, so that they shall accurately touch those planes in directions perpendicular to the edge at which they meet; and the alternate and opposite angle, which of course coincides with that of the crystal, is read off in the degrees of the graduated arc.

Fig. 53.



(80) *Reflecting Goniometer.*—A far more elegant and accurate instrument is the *reflecting goniometer* of Wollaston, fig. 55. The principle upon which it acts may be thus explained:—Let *a b c d* (fig. 54), represent a section of the crystal to be measured. A ray of light, *i r*, reflected as at *r s*, from the surface of the crystal, forms the radius of the arc which is to be measured. One plane, *a b*, of the crystal is brought into a fixed position with regard to the graduated circle, and the inclination of the two planes, *a b*, *b c*, is ascertained by measuring the arc which the graduated limb of the instrument describes, in order to bring the second plane, *b c*, of the crystal into the same position as the first, *a b*. The *supplement*, *a b c*, of this arc, E *c*, measures the inclination of the two planes. The angle may, however, be read off at once, by attending to the following instructions:—

Fig. 54.

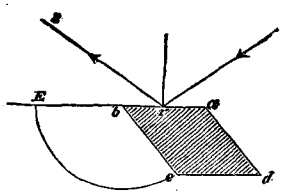
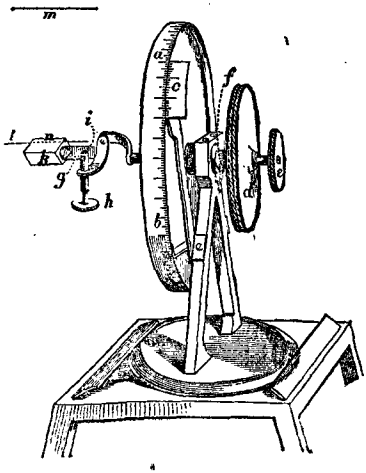


Fig. 55.



The instrument (fig. 55) consists of a brass disk, *a b*, supported in a vertical plane, and graduated on its outer edge to half degrees. By means of a milled head, *d*, this disk may be turned round in its own plane; the angle through which it has been made to turn is read off by a vernier, *c*, which is permanently fixed. The axis, *f*, of the graduated circle is pierced by a second axis, attached to the milled head, *e*, which is intended to give

rotation to the parts supporting the crystal, independently, when necessary, of the movements of the graduated circle, *a b*.

'To use the goniometer, it should first be placed on a pyramidal stand, and the stand on a small steady table, placed about six to ten or twelve feet from a *flat* window. The graduated circular plate, *a b*, should stand *accurately* perpendicular to the window, the pin, *h i*, being horizontal, with the slit end, *i*, nearest the eye. Place the crystal which is to be measured on the table, resting on one of the planes whose inclination is required, and with the edge at which those planes meet the farthest from you, and parallel to the window in your front. Attach a portion of wax to one side of the small brass plate, *g*; lay the plate on the table with one edge parallel to the window, the side to which the wax is attached being uppermost, and press the end of the wax against the crystal, *k*, till it adheres; then lift the plate, with its attached crystal, and place it in the slit of the pin, *h i*, with that side uppermost which rested on the table.

'Bring the eye now so near the crystal, as, without perceiving the crystal itself, to permit your observing distinctly the images of objects reflected from its planes; and raise or lower that end of the pin which has the small circular plate, *h*, attached to it, until one of the horizontal upper bars, *m*, of the window is seen reflected from the upper or first plane of the crystal, and till the image of the bar, *n*, is brought nearly to coincide with some line, *l*, below the window; as the edge of the skirting-board where it joins the floor. Turn the pin, *h i, on its own axis*, if necessary, until the reflected image of the bar of the window coincides accurately with the observed line below the window. Turn now the small circular plate, *e*, on its axis, and from you, until you observe the same bar of the window reflected from the second plane of the crystal, and nearly coincident with the line below; and having, in adjusting the first plane, turned the pin on its axis to bring the reflected image on the bar of the window to coincide *accurately* with the line below, now move the lower end of that pin *laterally* either towards or from the instrument, in order to make the image of the same bar reflected from the second plane coincide with the same line below.

'Having assured yourself, by looking repeatedly at both planes, that the image of the horizontal bar reflected successively from each, coincides with the same line below, the crystal may be considered as adjusted for measurement. Let the 180° on the graduated circle be now brought opposite the 0° of the vernier, by turning the middle plate, *d*, and while the circle is maintained accurately in this position, bring the reflected image, *n*, of the bar, *m*, from the first plane, to coincide with the line, *l*, below, by turning the small circular plate, *e*. Now turn the graduated circle from you, by means of the middle plate, *d*, until the image of the bar reflected from the second plane is also observed to coincide with the same line.' (Brooke's *Crystallography*, p. 30.) In this position, the reading of the vernier gives at once the inclination of the two planes to each other. It is almost superfluous to remark that the reflecting goniometer can only be applied in cases in which the surfaces of the crystal have sufficient polish and brilliancy to reflect the image of the line by means of which the angle is read off.

(81) *Symmetry of Crystalline Form.*—The study of the geometrical relations of different crystalline forms to each other belongs to the science of crystallography. It will be sufficient for the present purpose to indicate the general principle upon which the classification of crystals is founded. This principle is the symmetrical arrangement upon which every crystalline form is constructed. Symmetry, or a complex uniformity of con-

figuration (that is, similarity in the arrangement of two or more corresponding forms round a common centre), is the general law of creation, both in the vegetable and animal kingdoms. It is exhibited in the correspondence in external form of the right and left side of the body in animals, in the similar arrangement of the leaf on either side of its midrib, in the two lobes of the dicotyledonous seed, and indeed it attracts the notice of every observer in numberless cases. The same law holds good still more rigidly, though not so obviously, in the constitution of every crystal. If one of the primary planes or axes of a crystal be modified in any manner by molecular forces acting within the liquid or the crystal, all the symmetrical planes must be modified in the same manner.

The imaginary line which thus governs the figure, and about which all the parts are similarly disposed, and with reference to which they correspond exactly, is termed the *axis of symmetry* in a crystal. If a rhombohedron of Iceland spar be held with one of its obtuse angles uppermost, the vertical line which joins that angle to the opposite obtuse angle is the axis of symmetry of the crystal. Each extremity of the axis is formed by the meeting of three planes, each similar to the others, and all inclined to the axis at an equal angle. If any internal molecular force produce the replacement of any of the edges of one of those faces, the same cause must act with similar intensity upon the corresponding edge of the other faces, and produce a corresponding modification. The variation thus introduced into the form of the crystal has a symmetrical character; and the alteration, which is experienced by each of the three divisions of which the crystal consists, is consequently similar in each case.

There are, however, crystals that possess more than one axis of symmetry; and an arrangement of crystalline form, first proposed by Weiss, and which is now universally adopted, is based upon the relation which these axes bear to each other. These axes, it must be remembered, are *imaginary* lines, which connect the opposite angles or faces of a crystal, and all of them intersect each other in the centre of the figure. In the regular system, to which the cube, the regular octohedron, and rhombic dodecahedron belong, there are three axes, which are all equal, and cross each other in the centre of the crystal at right angles. If one of the faces or edges upon any of these equal axes be modified, not only are all the faces or edges upon that axis similarly modified, but all the faces and edges of the entire crystal experience a similar modification; since the symmetry of all the

axes is alike, and the molecular modifying force acts equally upon all. But this rule, though of very general application, is not without exception. If, for instance, a crystal rest upon one face during its formation, the mechanical obstacle to its symmetrical development is frequently the cause of considerable interference with the regular growth in this direction, but this interference does not operate upon the upper and exposed faces. This interference of causes external to the crystal is very generally observed in crystalline masses artificially obtained (75). The crystals of which the mass is composed cross each other in all directions, and form a confused structure, from the surface of which project isolated crystals, one extremity only of which is developed regularly.

Some minerals occur in forms termed *pseudomorphous* (from ψεῦδος, a falsehood, μορφή, form); that is to say, they exhibit forms which are not truly related to their own crystalline system. Such pseudomorphous crystals are formed by deposition in cavities previously occupied by crystals of a different nature, but which have been slowly dissolved out of the mass in which they were included, leaving spaces corresponding to their form; and during the process of the solution of the original crystal, or after its completion, the new compound has gradually taken the place, and adapted itself to the form, of the crystal which has undergone removal, as when, for example, quartz is found in the form of heavy spar, fluor spar, calc spar, or plumbic sulphate.

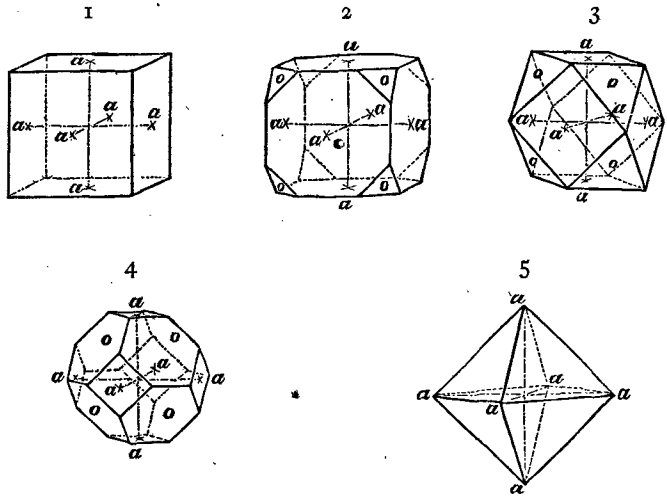
(82) *Classification of Crystals.*—Crystals are subdivided into six classes or systems, founded upon the relation of their axes of symmetry to each other. These relations exert an influence not only upon the geometrical connexion of the forms of crystals, but also upon their optical and physical properties. It is necessary in studying crystalline forms, the relations of which are often very complicated, always to place the crystal in a definite position. It will be found most convenient to place the principal axis in a vertical direction. The observance of this rule greatly facilitates the comparison of the compound with the simple forms.

The six classes into which crystals are subdivided are the following:—1st, the Regular or Tessular system; 2nd, the Right square prismatic, or pyramidal; 3rd, the Rhombohedral; 4th, the Prismatic; 5th, the Oblique; 6th, the Doubly oblique.

1. *The Regular,* or *Tessular,* or *Cubic System,* is characterized by three equal axes, *a a, a a, a a,* figures 56, 57, 58, around which the crystals are symmetrically arranged: crystals of this class are hence often designated as *monometric:* the three axes

cross each other at right angles. Crystals belonging to this system expand equally in all directions when heated, and refract light simply. The most important varieties of simple forms are the cube, as shown in fluor spar, common salt, and iron pyrites (fig. 56, 1): the octohedron (fig. 56, 5), exemplified by alum and

Fig. 56.



Passage of the Cube to the Octohedron.

magnetic iron ore; the tetrahedron (fig. 58, 3), sometimes seen in copper; and the rhombic dodecahedron (fig. 57, 3), as in the garnet and cobalt sulphide. Upon the geometrical relations of these forms, a single instance showing one of the simplest cases of such a connexion will suffice:—

From the cube may readily be deduced the three other allied forms of the regular system. By truncating each of the eight solid angles by planes equally inclined to the three adjacent faces of the cube, we obtain the *octohedron*, in which the three axes of the cube terminate in the six solid angles of the figure, one of which consequently corresponds to the centre of each side of the cube. (See fig. 56.) The faces marked *o* are those of the octohedron.

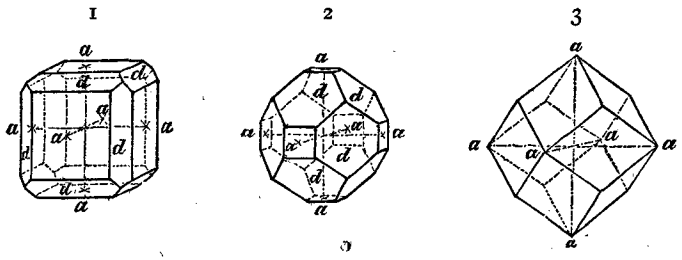
By replacing each of the twelve edges, *d d d*, of the cube, we arrive at last at the *rhombic dodecahedron*. (Fig. 57.)

By truncating the alternate angles, *t t*, we obtain the *tetrahedron*, as shown in fig. 58.

Homohedral, or *Holohedral* forms, are those which, like the

cube and octohedron, possess the highest degree of symmetry of which the system admits. *Hemihedral* forms, on the other

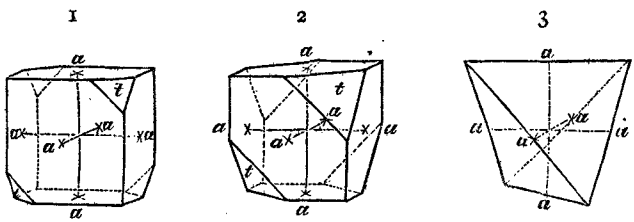
FIG. 57.



Passage of the Cube to the Dodecahedron.

hand, are those which may be derived from a holohedral form, as the tetrahedron is from the octohedron (fig. 50), or from

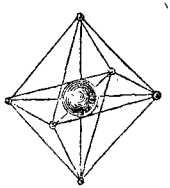
FIG. 58.



Passage of the Cube to the Tetrahedron.

the cube (fig. 58), by supposing half the faces of the holohedral form omitted, or its alternate angles or edges replaced, according to a certain law. Again, if half the faces of a hemihedral crystal be omitted, a *tetartohedral* form is the result.

FIG. 59.

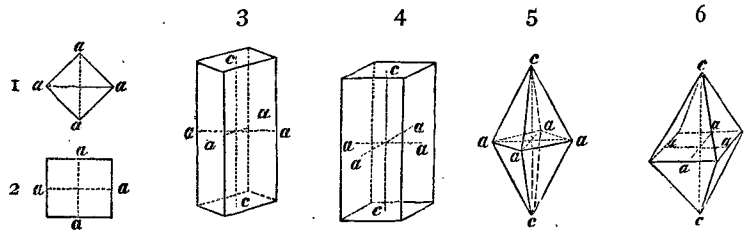


These relations will be readily traced, even by those unacquainted with geometry, by cutting out two or three cubes in soap, or some other sectile body, and paring down the angles or edges in the manner above described.

In a similar manner, by inserting wires into an apple (fig. 59), we may represent to the eye the direction assumed by each of the axes of a crystal; and by winding a piece of thread round each point of the wires, and stretching the thread across from one wire to another, the outline of an octohedron belonging to any of the systems is readily obtained.

2. *The Right Square Prismatic,* or *Pyramidal System.*—In this system there are three axes, all at right angles to each other, but two only, *a a*, *a a* (fig. 60), are equal; the third, *c c*, being either longer or shorter than the others. The crystals of this class, from this circumstance, are said to be *dimetric.* Generally there is no simple relation between the length of the axis, *c c*, and that of the other two. Expansion by heat is equal in two directions. The crystals of this system have only one axis of single refraction, *c c* (117, 118), as they, as well as those of the four other systems not yet described, exert double refraction on light.

FIG. 60.



Pyramidal, or Right square Prismatic System.

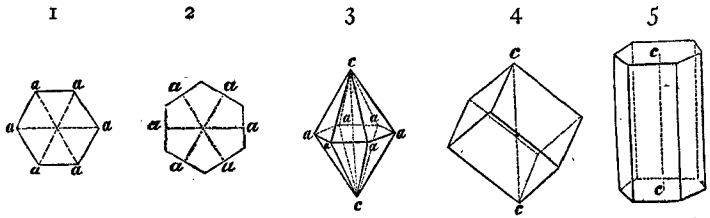
Four principal forms belong to this system—viz., two prisms with a square base, and two octohedra. The prisms differ from each other according as the equal axes, *a a*, *a a*, terminate in the angles of the base, as seen in fig. 60, 1; or in the sides of the base, as at 2. Similar differences exist in the two octohedra. The octohedron is said to be *direct,* when the axes end in the angles, and *inverse,* when they end in the edges. 3 represents a right square prism the axes of which terminate in the edges of the crystal; in 4, the axes terminate in the sides of the prism; 5 is the direct octohedron, with its axes in the solid angles; 6, the inverse octohedron, with the axes in the edges. Examples of this system are seen in potassic ferrocyanide, mercuric cyanide, tinstone, and anatase.

In consequence of the absence of any fixed relation in length between the principal axis, *c c*, and the other two axes, in the four different prismatic systems, these prisms may vary in length indefinitely. In some cases, the axis, *c c*, is so short that the crystal assumes the form of a flattened plate, when it is said to be a *tabular* crystal; in others it forms a long prism of indefinite length. In the octohedron of the various prismatic systems, the principal axis, *c c*, does not, even in the same compound, always bear

the same proportion in length to the other two axes; though in these various octohedra, the axis, *c c*, always bears some simple ratio in length to those of the other octohedra of the same body.

3. *The Rhombohedral*, or *Hexagonal System.*—In this system there are four axes; three of them, *a a*, *a a*, *a a*, are of equal lengths, are situated in the same plane, and cross each other at angles of 60°; whilst the fourth, *c c*, is perpendicular to these, and may vary in length. The crystals of this class produce, in a very marked manner, the effects of double refraction on light. They have one axis, *c c*, of single refraction; and by the application of heat expand equally in two directions. In this system the principal forms (fig. 61) are the bi-pyramidal dodecahedron,

FIG. 61.

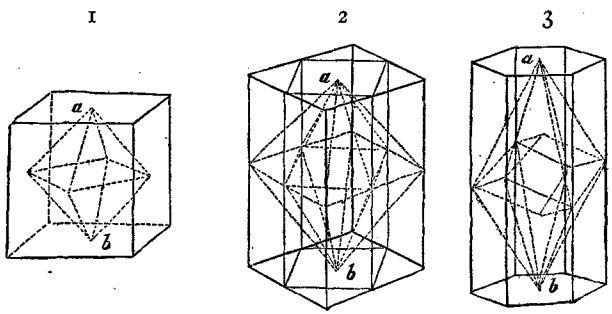


Rhombohedral System.

3, (of which there are two varieties, according as the axes terminate in the angles of the base, 1, when it constitutes a direct dodecahedron; or in its sides, 2, when the dodecahedron is said to be inverse); the rhombohedron, 4, and the six-sided prism, 5. Of each of these forms there are likewise two varieties, depending upon the position of the axes. 4 is an inverse rhombohedron. Among crystals which belong to this system are ice, quartz, beryl, Iceland spar, and sodic nitrate.

Fig. 62 represents, in one view, the manner in which the

FIG. 62.

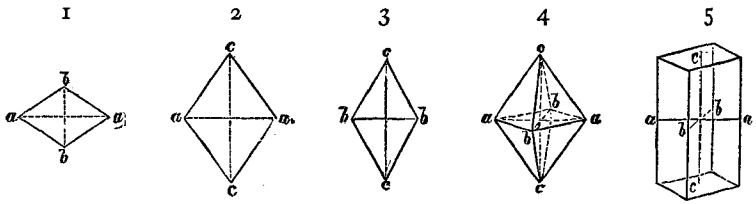


principal forms in each of the first three systems can be described about the crystallographic axes. 1 exhibits the octohedron inscribed in the cube; 2 shows both varieties of the octohedron and of the square prism; 3 the six-sided prism, containing the rhombohedron and bi-pyramidal dodecahedron.

The relations of the first three systems are simple, and easily traced; the other three systems are more complicated, owing to the variety introduced by the irregular lengths and obliquities of the axes.

4. *The Right Rectangular Prismatic,* or *Prismatic System.*—The crystals of this system have three axes, *a a, b b, c c* (fig. 63),

FIG. 63.



Prismatic, or Right Rectangular Prismatic System.

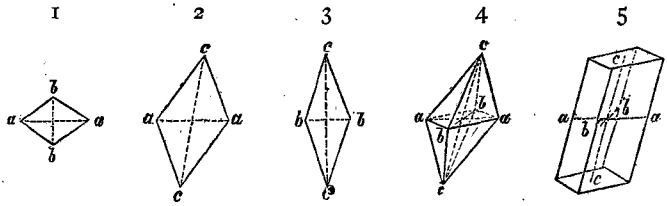
all at right angles to each other; each axis differs from the others in length, and they usually bear no simple proportion to each other. Crystals of this class are hence termed *trimetric* by some writers. In this and in the two remaining systems, the crystals expand unequally by the application of heat, in the three directions of these axes; and they have two other resultant axes in which there is no double refraction (118).

The principal varieties of the prismatic system are the right octohedron with a rhombic base (fig. 63, 4), or right rhombic octohedron; and the right prism with a rhombic base or right rhombic prism, 5. Both these figures have a rhombic base, 1; the axes terminate in the solid angles of the octohedron, and in the edges of the prism. Owing to the inequality in the lengths of the axes, the sections of the octohedron through *a b a b*, 1, *c a c a*, 2, and *c b c b*, 3, though all rhombic in form, are each different in dimensions. The faces of the octohedron are all equal, but the length of each side of its triangular faces is different. To this class belong nitre, aragonite, topaz, baric sulphate, and sulphur obtained by evaporation from carbonic disulphide.

5. *The Oblique,* or *Monoclinic System.*—The three axes of this system may all differ in length; two of them, *c c, a a,* cross

each other obliquely (fig. 64, 2); the third, *b b*, is perpendicular to both the others; generally there is no simple proportion between the lengths of the different axes. The principal forms are the oblique octohedron with a rhombic base, 4, and the oblique

Fig. 64.

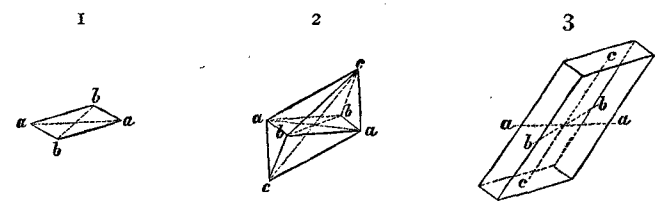


Oblique System.

rhombic prism, 5, in both of which the axes are in the angles of the crystal. The base of the figure in each case is a rhombus, 1, in which the axes *a a*, *b b*, cross each other at right angles. In the octohedron, the section through the two oblique axes, *a a*, *c c*, 2, is a rhomboid; the axis, *c c*, crosses the third axis, *b b*, perpendicularly, and a section through these axes produces the rhombus shown in 3. The octohedron of this system is not perfectly symmetrical. Each of the three sides forming its triangular faces differs from the others in length, and the faces are of two kinds. The two upper front faces of 4, fig. 64, correspond to the two lower back faces, and the other four faces are alike. Besides the oblique rhombic octohedron, there are three forms of the oblique rhombic prism; the kind of prism being defined by the axis with which the long axis of the prism coincides. Sodic sulphate, hydric disodic phosphate, sulphur crystallized by fusion and slow cooling, borax, and ferrous sulphate offer examples of crystals belonging to this class.

6. *The Doubly Oblique, Triclinic,* or *Anorthic System.*—In this system each of the three axes may differ from the others in length, and all cross each other obliquely. The principal varieties

Fig. 65.



Doubly Oblique, or Anorthic System.

of crystalline form are the doubly oblique octohedron (fig. 65, 2), the base of which is seen at 1, and the doubly oblique prism, 3. The octohedron is not symmetrical in its form: its four upper faces are all alike, but each face corresponds to the lower face which is parallel to it. Cupric sulphate and bismuth nitrate belong to this class, which, however, contains comparatively few substances. Some of the varieties of crystalline forms which it includes are very complicated, and difficult to define.

Isomorphism—Dimorphism—Allotropy.

(83) *Isomorphism.*—Owing to the comparatively small number of forms which belong to the regular system, and to the perfect symmetry which characterizes them, it necessarily happens that a variety of bodies, very dissimilar in properties and in chemical composition, assume crystalline forms which are not distinguishable from each other, since they coincide exactly in their angular measurements. For example, the elements—carbon, gold, and copper, and the compounds—plumbic sulphide, iron pyrites, fluor spar, alum, and spinelle, all crystallize in cubes or octohedra which perfectly resemble each other; yet these substances present no similarity to each other either in properties or in chemical composition.

Crystals which belong to the other systems, however, do not so frequently present this exact similarity in form; for though they may crystallize in similar prisms or octohedra, yet a measurement of the angles will suffice to show considerable differences in the length of the axes, and, in the case of the two oblique systems, in the inclination of the axes to each other. But in these systems likewise, as well as in the regular system, cases occur in which an exact, or almost exact identity in crystalline form, even in these respects, is found. In the larger number of these instances, as Mitscherlich has proved, the chemical composition of the substances which thus correspond in form is analogous. Bodies which possess this similarity in form are termed *isomorphous* (from ἴσος, equal, μορφή, form). The term isomorphous is, however, restricted to such substances as exhibit not only similarity in form, but at the same time, the analogy in their chemical composition just alluded to. The diamond (C), magnetic oxide of iron (FeO, Fe_2O_3), and alum (K_2Al_2 4 SO_4, 24 H_2O), all crystallize in octohedra, yet they are not usually cited as instances of isomorphism: but the spinelle-ruby (MgO, Al_2O_3), magnetic oxide of iron (FeO, Fe_2O_3), and chrome-iron ore (FeO,

Cr_2O_3), not only crystallize in the same form, but have a constitution perfectly analogous, and are therefore truly isomorphous. Mitscherlich, indeed, endeavoured to show that crystalline form is independent of the chemical nature of the atoms, and that it is determined only by their grouping and relative position; the same number of atoms combined in the same way, always producing the same crystalline form.

This statement is not strictly true: the elementary bodies have by no means all of them the same crystalline form, which may be due to their molecules possessing different atomic structures; and it is found that even when the chemical constitution is the same, though there may frequently be a close similarity in the form assumed, yet a careful measurement of the angles indicates differences in the length or inclination of the axes. For example—the carbonates of calcium, manganese, magnesium, iron, and zinc, all crystallize in rhombohedra; but the corresponding angles of these several crystals are all different, as the following table shows:—

Calcic carbonate (calc spar) . .	$CaCO_3$.	105° 5′
Manganous carbonate (diallogite) .	$MnCO_3$.	106° 51′
Ferrous carbonate (chalybite) . .	$FeCO_3$.	107° 0′
Magnesic carbonate (magnesite) .	$MgCO_3$.	107° 29′
Zincic carbonate (calamine) . .	$ZnCO_3$.	107° 40′

These differences are in all probability partially due to differences in the crystalline arrangement of the elementary molecules of some of the components, and, as Kopp has shown, in the atomic volume or space occupied by these ultimate molecules. The crystals of metallic zinc and iron, for instance, belong to different systems, so that it is not surprising that some difference should be observed in the form of their corresponding compounds; and if Mitscherlich's law be confined to compound bodies, these very differences which have been supposed to militate against it, will prove to be remarkable corroborations of its truth, as they show that the number and collocation of the atoms may overcome the tendency of some of the atoms of the elementary components to assume different forms. It also shows, moreover, that it is unsafe to infer isomorphism in the elements simply from the occurrence of isomorphism in the compounds which they yield. It must, however, be borne in mind that bodies which are analogous in chemical composition and in properties, are not necessarily isomorphous: for example, magnesic carbonate ($MgCO_3$) crystallizes in

rhombohedra, whilst strontic carbonate ($SrCO_3$) assumes the form of oblique rhombic prisms.

It not unfrequently happens that a compound group like ammonium (H_4N), if equivalent in function to a simple substance like potassium (K), will form compounds with the acid radicles, which are isomorphous with those of the simple substance with the same radicles; this is manifest in potassic chloride (KCl) and ammonic chloride (H_4NCl), both of which crystallize in cubes. Potassic sulphate (K_2SO_4) is in like manner isomorphous with ammonic sulphate [$(H_4N)_2SO_4$], and so on through the greater number of the corresponding compounds of potassium and ammonium.

(84) *Chemical Bearings of Isomorphism.*—This discovery of the coincidence of similarity in crystalline form with similarity in chemical composition, is one of the most important generalizations yet arrived at in the science of crystallography. It has rendered great service to chemistry by facilitating the classification of compounds, and it has often called attention to analogies in composition which might otherwise have been overlooked. In determining the atomic weight of a substance it is also frequently of essential value; but its application to these purposes will be more advantageously examined at a future period.

Bodies which approach each other thus closely in crystalline form often occur mixed together in variable proportions in regularly crystallized minerals. Such isomorphous compounds cannot be separated by the method of crystallization. Indeed it is quite possible to obtain crystals consisting of alternate layers of different isomorphous salts, if they have nearly the same degree of solubility in water. An octohedral crystal of ordinary alum, for example, if transferred to a solution of chrome alum (a compound isomorphous with ordinary alum, and which differs from it in containing chromium in the place of aluminium), will continue to increase in size regularly, and a layer of the metallic salt will be deposited on the common alum. If the crystal be transferred again to the original solution of alum, a fresh layer of colourless alum will be formed upon the chromium salt, and so on in succession.

A large number of metals, when united with the same acid radicle, furnish salts which are isomorphous. For instance, the sulphates of magnesium, zinc, iron, nickel, cobalt, manganese, and cadmium, all crystallize in similar forms. The isomorphism of many acid radicles, when united with the same metal, such as potassium or sodium, is not less evident: sulphate, seleniate,

chromate, and manganate of potassium, all have the same form; and the isomorphism of the corresponding phosphates and arseniates of sodium is equally striking.

(85) The following table exhibits some of the more important of the groups in which the existence of isomorphism has been distinctly ascertained :—

ISOMORPHOUS GROUPS.

(*A.*) *Elements.*

1	2
Diamond	Arsenic
Lead	Antimony
Iron	Bismuth
Copper	Tellurium (?)
Silver	
Gold	
Cadmium	
Mercury	
Palladium	

(*B.*) *Compounds.*

3		6	
Alumina	Al_2O_3	Sulphides*	
Ferric oxide	Fe_2O_3	Arsenides	
Chromic oxide	Cr_2O_3	Antimonides	
Ilmenite	$(FeTi)_2O_3$		
4		**7**	
Arsenious anhydride ...	As_2O_3	*Potassium-compounds of*	
Antimonious oxide ...	Sb_2O_3	Chlorine	KCl
		Iodine	KI
5		Bromine	KBr
Tinstone	SnO_2	Fluorine	KF
Rutile	TiO_2	Cyanogen	KCy

Salts of the following Acid Radicles when united with the same Metal M′ *representing any Monad or Monobasic Metal.*

8		10	
Phosphates	M'_3PO_4	Molybdates	M'_2MoO_4
Arseniates	M'_3AsO_4	Tungstates	M'_2WO_4
		Chromates (in the unusual form of Plumbic chromate)	$Pb''CrO_4$
9			
Sulphates	M'_2SO_4	**11**	
Seleniates	M'_2SeO_4	Perchlorates	$M'ClO_4$
Chromates	M'_2CrO_4	Permanganates	$M'MnO_4$
Manganates	M'_2MnO_4		

* It appeared to be anomalous, upon the earlier supposition that the atomic weight of sulphur was 16, that 32 parts of sulphur should be isomorphous with 75 of arsenic, two atoms of sulphur apparently being isomorphous with one of arsenic; but if the atomic weight of sulphur is admitted to be 32, the anomaly disappears. A similar remark applies to the permanganates and perchlorates, if the atomic weight of manganese be taken as 27·5. The permanganates would

Salts of the following Metals when united with Equivalent Quantities of the same Halogen or Acid Radicle.

12	13
Magnesium	Barium
Calcium (in Calc Spar)	Strontium
Zinc	Calcium (in Aragonite)
Cadmium	Lead
Iron	
Manganese	14
Cobalt	*Double Chlorides of*
Nickel	Platinum ... ... $2\,KCl,PtCl_4$
Copper	Osmium ... ... $2\,KCl,OsCl_4$
Lead (in Plumbo-calcite)	Iridium ... ... $2\,KCl,IrCl_4$

15

Potassium Ammonium

(86) *Dimorphism.*—Another very remarkable fact connected with crystallization has been observed in a few bodies. Some substances, sulphur, for example, are capable of assuming two dissimilar forms, according to the temperature at which the crystals are produced. Sulphur, as it is found crystallized in nature, or as it is obtained by the spontaneous evaporation of its solution in carbonic disulphide or in chloride of sulphur, is deposited in the form of octohedra with a rhombic base, which is one of the forms of the 4th, or prismatic system. When obtained by the slow cooling of a mass of melted sulphur, beautiful amber-coloured prismatic crystals are obtained, belonging to the 5th, or oblique system. These oblique prisms, in the course of a few days, at the usual atmospheric temperature, become opaque, lose their cohesion, and are gradually converted into a congeries of octohedra. A similar change is produced in the octohedral crystals by exposing them for some time to a heat of about 110° C., but the opacity is in this case due to the formation of prismatic crystals. The crystalline axes of the two forms differ, and consequently the crystals belong to different systems. Bodies capable of thus assuming two forms geometrically incompatible are said to be *dimorphous.*

Many other instances might be mentioned. Carbon, in its pure state, as it occurs in the diamond, is crystallized in the 1st, or regular system, in octohedra, or in allied forms; but in graphite, as it separates from cast iron when fused, it assumes the shape of

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then appear to contain two atoms of manganese, whilst the perchlorates contain only one of chlorine; but assuming, as we have done, on other grounds, that the atomic weight of manganese should be doubled, or should be 55, then it follows, as a matter of course, that the number of atoms of manganese and chlorine are alike in the two compounds.

six-sided plates, which belong to the rhombohedral system. Calcic carbonate usually occurs in forms of the 3rd system, reducible by cleavage to rhombohedra, like those of Iceland spar, and it is thus formed by crystallization at low temperatures; but occasionally it occurs in the rectangular prisms of the 4th system, as in the mineral aragonite; and the microscopic crystals which are formed when calcic carbonate is deposited from its solution by carbonic acid in water, on the application of a heat of 100° C., have also this form (G. Rose). Another beautiful instance of dimorphism is afforded in mercuric iodide. When this body is heated, it fuses, boils, and is converted into vapour, which condenses upon the side of the tube as a yellow crystalline crust, composed of minute rhombic plates. Slight friction, such as a mere scratch upon a single point, changes the form from the rhombic plate to that of an octohedron with square base, and the change is rendered visible to the eye by the accompanying substitution of a bright scarlet for the yellow colour. If the quantity of the iodide operated on be at all considerable, the temperature of the mass may be observed to rise as much as 3° C. during the conversion of the yellow into the red salt (Weber).*

In certain cases the forms of a crystal belonging to one system may approach very closely to those of crystals belonging to a totally different system: for instance, bismuth appears to crystallize in cubes, but in reality it assumes the form of a rhombohedron, the angles of which are 92° 20′, and 87° 40′, or so close upon right angles, as to ordinary observation to be confounded with them: the derivative forms, however, in such cases are always very different, and generally enable the observer to point out the true system to which the crystal belongs.

According to the observation of Pasteur, instances of dimorphism usually occur when one of the two forms is nearly upon the limit of the system to which it belongs (*Ann. Chim. Phys.* 1848 [3], xxiii. 271). For example, the angles of the yellow rhombic plates of mercuric iodide do not differ much from those of the octohedron of the prismatic system to which the red variety of this compound belongs, and a similar remark is applicable to the prisms and the octohedra of sulphur.

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* The following substances, according to Professor W. H. Miller, are also dimorphous:—Titanic anhydride, prismatic in brookite, pyramidal in rutile; ferric disulphide, cubic in ordinary pyrites, prismatic in white pyrites (marcasite); potassic sulphate, usually prismatic, sometimes rhombohedral; nitre, usually prismatic, sometimes rhombohedral; diarsenide of nickel ($NiAs_2$), usually cubic, but prismatic in the white variety.

Some substances are stated to be even *trimorphous*, that is, they crystallize in three different systems. Both zincic seleniate ($ZnSeO_4$, 7 H_2O) and zincic sulphate ($ZnSO_4$, 7 H_2O), and nickel seleniate ($NiSeO_4$, 7 H_2O) and nickel sulphate ($NiSO_4$, 7 H_2O), according to Mitscherlich, exhibit this peculiarity. Nickel sulphate crystallizes below 15° C. in right rhombic prisms; between 15° and 20° C. in acute square-based octohedra; and when the temperature is above 30° C. in oblique rhombic prisms. In the first case the crystals belong to the prismatic, in the second to the pyramidal, and in the third to the oblique system. If the right rhombic crystals be placed in the summer's sun for a few days they become opaque, but still retain the form of the prism, which is found, when broken, to consist of a mass of octohedra.*

It is not unlikely that the change of tenacity produced in some of the metals by elevation of temperature, and exhibited in a marked degree by zinc, is produced by some modification of their crystalline form under the action of heat.

The influence of temperature in thus subverting the direction of the molecular attractions in obedience to which crystals are formed, has as yet scarcely been made the subject of systematic research; its further prosecution, however, cannot fail to throw much additional interesting light upon our knowledge of the operation of molecular attraction.

In certain cases two isomorphous bodies are similarly dimorphous, or *isodimorphous*, such, for instance, as arsenious anhydride and antimonious oxide, both of which crystallize in regular octohedra and in four-sided prisms; palladium and iridium, as well as potassic and sodic nitrates, which all crystallize in rhomboidal prisms or in hexagonal prisms; cuprous and argentic sulphides, which occur either in cubes or in rhomboidal prisms.

(87) *Allotropy.*—Independently of dimorphism, the particles of many solids are capable of other modes of arrangement, which, without altering the chemical composition of the body, yet produce a very important modification of many of its properties, both chemical and physical.

There appear to be four different conditions in which solid bodies may exist. They may be—1st, *crystalline*, as diamond, garnet, felspar; 2nd, *vitreous* or glassy, as glass itself, transparent arsenious anhydride, and barley sugar; 3rd, *amorphous*, or destitute of crystalline form altogether, as tinder, chalk, or clay; and 4th, *organized*, or arranged in masses, consisting of cells, fibres, or membranes, like the tissues of animals or vegetables, as hair,

* According to De Marignac, however, nickel sulphate in the second and third forms contains 1 H_2O less than it does when crystallized in right rhombic prisms; and if this be true for nickel sulphate, it is most probably the case with the other salts above mentioned as trimorphous.

muscle, skin, wood, bark, leaves, &c. To these organized structures no further allusion will for the present be made, since they are producible only by the living organism.

Many substances are capable of assuming indifferently any one of the first three of these conditions. Sulphur, for example, often occurs naturally in beautiful octohedral crystals, and may always be obtained in this form by allowing its solutions to evaporate spontaneously in the air. These crystals are hard and brittle, and they may easily be dissolved in carbonic disulphide. But if a quantity of these crystals be melted, and heated considerably beyond the boiling point of water, and the liquid be then suddenly cooled by pouring it into cold water, a tough, flexible, transparent substance, of an amber colour, is procured, which may be kneaded in the hand or drawn out into long threads, and is less easily inflamed than ordinary sulphur. This constitutes vitreous sulphur; but if it be left for a few days, it becomes brittle, opaque, and partly crystalline. However, it is not all crystallized, for if digested with carbonic disulphide, part of it only will be dissolved; the crystallized portion is taken up, and a buff-coloured powder is left, which is insoluble. It has no crystalline appearance, and is amorphous sulphur. This, if melted by heat, becomes as soluble as before. In addition to these alterations in consistence, colour, inflammability, and solubility, differences in the density are observed:—

Octohedral sulphur has a density relative to water of				2·05
Prismatic sulphur	„	„	„	1·955
Vitreous sulphur	„	„	„	1·957

Corresponding differences in the specific heat have been observed in these different conditions.

These three different forms of sulphur are called *allotropic* modifications of sulphur, and the existence of the same substance in different forms, each endowed with different properties, is called *allotropy* (from ἄλλος, another, and τρόπος, manner).

Phosphorus affords another excellent instance of this singular series of modifications. Phosphorus, when first prepared and as sold in the shops, is in the form of transparent, flexible, waxy-looking sticks which are of the vitreous variety. In this form it is freely soluble in carbonic disulphide, melts in warm water at a temperature very little above that of the human body, and is so inflammable, that if left exposed to the air, even for a few minutes, in warm weather, it often takes fire and burns with great violence. Phosphorus has also been obtained in crystals,

which are equally inflammable with the common form. But if phosphorus be put into a flask filled with nitrogen or carbonic anhydride, to prevent it from taking fire, and be heated, with various precautions to avoid accident, up to the melting point of tin (228° C.), or rather higher, in a few hours it will be changed into a red powder which, when properly purified, may be exposed to the air without any danger of taking fire. In this condition it does not melt until heated to 500° (260° C.), or even beyond that temperature; and it is quite insoluble in carbonic disulphide. Yet it is pure phosphorus, although in the amorphous condition. By heating it to about 572° (300° C.), in a retort or vessel from which the air is excluded, it melts, and then cannot be distinguished from the original phosphorus that furnishes it. In addition to these alterations in solubility, colour, inflammability and external appearance, differences in the density and in specific heat have been observed.

Many other elementary bodies exhibit analogous allotropic modifications, and their number will no doubt be increased as researches in this direction become multiplied. It is probable, indeed, that such modifications exist in all the elements, although the properties of the different forms are certainly not always so dissimilar as in the cases already quoted. Even in permanent gases we have indications of allotropy, the remarkable substance ozone having been ascertained to be oxygen in a particularly active condition, its molecule consisting of three atoms of oxygen, ordinary oxygen containing only two. The formation of this allotropic modification by an alteration in the constitution of the molecule renders it probable that the explanation of allotropy must be sought in the atomic structure of the elementary bodies. The consideration of special instances of allotropy will be deferred until the properties of the bodies themselves are detailed. Allotropy does not appear to be confined to elementary bodies; but in compounds it is not always easy to determine whether the corresponding modifications may not be due to alterations in chemical composition, arising from a change in the mode of combination of the different component elementary bodies with each other.

It is certain, whatever be the causes which thus influence molecular arrangement, that the particular arrangement which such causes may produce in any given case, has a very material influence in modifying the physical properties of the body. When a body is homogeneous, or when it is symmetrically arranged, as in the crystals belonging to the regular system, the transmission

of light, the expansion by heat, and the conductivity of the body for heat, is uniform in every direction; but when the molecular attractions, as shown by the form of the crystal, are more powerful in one direction than in others, immediately a corresponding irregularity in the action of the body on light, and in its expansive and conducting powers for heat, may be traced. Wertheim has proved that the velocity of sound, when transmitted through wood, is nearly five times as great when transmitted in the direction of the fibre, as when transmitted across it; and Wiedemann (*Poyg. Ann.* 1849, lxxvi. 404) has shown that electric induction occurs with varying degrees of facility in different directions in the same doubly-refracting crystal.

CHAPTER IV.

LIGHT.

Nature of Light—Undulations—Reflection—Refraction—Production of Colour—Chemical Actions, Photography—Interference—Double Refraction—Polarization.

(88) *Chemical Relations of Light.*—The light which, operating through the eye, gives exercise to the sense of vision, until within the last few years, would have been thought to have little connexion with chemistry. Now, however, the case is otherwise, and an acquaintance with the fundamental laws and properties of light is indispensable to the chemist. The physical characters of an object, revealed by its action on light, are often of the greatest chemical value. Differences in refractive power, for example, furnish in many cases the most rapid and satisfactory proof of the genuineness or adulteration of an essential oil. Varieties in the amount and direction of circular polarization afford the best means in certain cases of arriving at a knowledge of the varieties and proportions of sugar in complex saccharine liquids. By the action of polarized light, the diamond and other precious gems may be distinguished from spurious imitations.

But besides the indirect assistance thus afforded to chemistry, the researches of the last sixty years have been gradually developing the vast importance of light as an agent in producing the chemical changes which are continually in operation upon the surface of the earth; and they have at length shown that this wonderful emanation from the sun is, conjointly with heat, the

mainspring which maintains the chemical actions, and with them the existence, of all the varied forms of organic life which teem around us. The fixation of carbon in the vegetable creation, the accumulation of materials for our habitations and for fuel, and the maintenance of a uniform composition in the atmosphere, may be mentioned in illustration of the importance of its chemical actions: whilst the fascinating art of photography gives proof of the rapidity and the variety of the changes which it produces; and in the new department of spectrum analysis we are furnished with a method of investigation which reveals to us the composition, not only of the flames of furnaces and of volcanoes, but even of the luminous atmosphere of the sun, the fixed stars, and the nebulæ, extending the range of our inquiries through distances limited only by that through which the object is visible.

The investigation of the laws of light belongs to the science of optics: in the following pages, therefore, reference will only be made to some of its principal properties, a knowledge of which will be a necessary preparation to the study of its chemical effects.

(89) *Sources of Light.*—1. The great natural sources of light are the sun and the heavenly bodies, but there are several modes of procuring light by artificial means. The other chief sources of light are the ignition of solids; phosphorescence by heat; luminous animals; phosphorescence of decaying animal matter; electricity; and certain cases of crystallization.

2. *Ignition of Solids.*—Whenever any solid object is raised to a high temperature (about 980° or 1000° F., equivalent to 526° or 538° C.), it becomes luminous. A current of gaseous matter may have a temperature of upwards of 2000° (1093° C.) without becoming luminous. If, however, a solid be introduced into such a current of heated gas, it begins to throw off light in all directions, even though it may not burn, and may experience no chemical change; under such circumstances, it is said to become *incandescent.* The colour of the light varies with the temperature. When first perceptible it is of a dull red colour, and as the temperature rises, it passes through orange and yellow into a full white, which, when the temperature becomes extremely high, assumes something of a violet tinge.

The experiments of Draper (*Phil. Mag.* 1847 [3], xxx. 345) show that platinum begins to emit light in the dark at a temperature which he estimates at about 977° (525° C.). He also found, by introducing different substances into a clean gun-barrel, and raising the barrel to a dull red heat, and then looking down into the barrel, that they all became red hot at the same time

within the barrel. The materials submitted to experiment were, platinum, brass, antimony, lead, and gas carbon; to these I may add, porcelain, black lead ware, copper, and palladium. Chalk and marble became visible before the barrel was red hot, and the phosphorescence of fluor spar was still more marked. At a temperature which, from the expansion of the platinum, Draper estimated at 1210° (659° C.), the light of a strip of platinum, heated by the voltaic current, was red, and extended up to the line F of the solar spectrum (106), where the colour of the emitted light was greenish grey. At 1325° (718° C.) the spectrum was prolonged into the bluish green. At 1440° (782° C.) the blue extended beyond Fraunhofer's line G; and at 2130° (1165° C.) a pure and intense spectrum, reaching as far as H, was obtained.

This observation may be carried still further by noting the effects produced upon the increase in the extent of the chemical action in the more refrangible portion of the spectrum, as the temperature is pushed still higher. The temperature of the voltaic arc and of the electric spark may thus be inferred greatly to transcend that of the sun and oxyhydrogen jet.

All our artificial lights depend upon the ignition of solid or dense gaseous matter, in the high temperature developed by the chemical changes attendant on combustion. One of the most remarkable instances of the production of light in this manner, is afforded by directing an ignited jet of mixed oxygen and hydrogen gases upon a piece of lime; the burning gas alone gives scarcely any sensible light, but as soon as the lime has become thoroughly heated, the brilliancy of the light is too great for the eye to bear.

3. *Phosphorescence by Heat.*—Some substances of mineral origin, when gently heated, emit a feeble light, which in a short time ceases, and cannot be again renewed until after the body has been exposed to the light of the sun, or to that emitted by the discharge of a Leyden jar (112). Native tricalcic diphosphate or phosphorite, and a variety of fluor spar known as chlorophane, exhibit the phenomenon very distinctly. Some organic compounds, such as quinine sulphate, and well-dried flour, particularly maize flour, also exhibit this phenomenon.

4. *Luminous Animals.*—The existence of phosphorescence may be recognised in the animal kingdom. The waters of the ocean in different parts of the globe, and at different times, appear to be luminous throughout, from the presence of countless hosts of luminous animalculæ: but usually the light of the sea appears to be developed only by agitation, and the crest of every wave may often be seen to be tipped with a beautiful fringe of pale green light. The glow-worm and the fire-fly offer other familiar instances of the same nature. Some kinds of scolopendra, in passing over the ground, leave a luminous trail behind them. Within certain limits, this power of emitting light appears to be under the control of the animal, and it ceases in a few hours after vitality is destroyed. Matteucci extracted from the glow-worm a yellowish phosphorescent matter, the light of

which became extinct at 18° (−8° C.), and recovered its luminosity as the temperature rose, but it disappeared when the temperature rose to 122° (50° C.). The presence of oxygen appears in this case to be necessary, as the luminosity is temporarily suspended by immersion in nitrogen, or in carbonic anhydride.

5. *Phosphorescence of Decaying Organic Matter.*—Sea fish, in general, and whiting, herring, and mackerel in particular, soon after death, exhibit a luminous appearance; the light is most intense before putrefaction commences, and gradually disappears as decomposition proceeds. In order to observe the phenomenon distinctly, the fish should be gutted, and the roes and scales removed. The entire fish, and especially the soft roe, exhibits the light. By placing such luminous fish in weak saline solutions, such as those of Epsom salts, Glauber's salts, or common salt, these solutions likewise become luminous, and the appearance continues for some days; it is particularly visible when the liquids are agitated. The light is quickly extinguished by the addition of pure water, of lime water, of fermented liquids, of acid and alkaline liquids, and of strong saline solutions in general: the saline solutions, however, on being diluted, recover their luminosity. If the fish be exposed to a cold sufficient to freeze it, the luminosity disappears, but it returns when it is thawed; luminous wood also ceases to emit light below 0° C. A temperature of about 100° (38° C.) seems to be that most favourable to the appearance of this remarkable light; it disappears considerably below 100° C., and the faculty of again becoming luminous on cooling is speedily destroyed by the continuance of the heat. (Hulme, *Phil. Trans.* 1800, 161.) This phosporescence does not appear to be dependent upon the process of oxidation, for Matteucci found that the light is not sensibly diminished by immersion in nitrogen, hydrogen, or carbonic anhydride.

6. *Electricity.*—The transient light of the electric spark, and the intense glare attendant on a flash of lightning, are familiarly known; but electricity may likewise be made to give a continuous and abundant supply of light: the ignition of charcoal-points between the wires of a voltaic battery may be made to yield a light which dazzles the unprotected eye. Attempts have been made to apply this light to the purposes of illumination on a large scale (280). Other less important sources of light, such as the friction of two pieces of quartz or of loaf sugar, may also possibly be of electrical origin.

7. *Crystallization.*—Light is likewise developed, under certain circumstances, in the act of crystallization. When the transparent form of arsenious anhydride is dissolved in hot hydrochloric acid, the liquid as it cools deposits crystals of opaque white arsenious anhydride: if the process be watched in a darkened room, the separation of each crystal will be seen to be accompanied by a faint flash. Fused sodic sulphate, and one or other vitrified salts, when dissolved in water and crystallized, exhibit the same phenomenon, which appears to accompany the transformation of a vitreous into a crystalline solid.

§ I. THEORIES OF LIGHT—REFLECTION—REFRACTION.

(90). *Theories of Light—Undulations.*—Two hypotheses have been proposed to account for the phenomena of light. Upon the first of these, the theory of *emission*, it is imagined that all

luminous bodies are constantly throwing off into space a luminous matter, the particles of which are inconceivably minute, and are projected with a velocity equally inconceivable. These particles, when they fall upon any object, are reflected more or less completely from its surface; and, entering the transparent portions of the eye, form images upon the retina or expanded termination of the optic nerve, and are by it transmitted to the brain; the result enabling us to see the object from which the light was scattered.

Upon the second hypothesis, that of *undulation*, recourse is had to the supposition of an elastic medium or ether of inconceivable tenuity, filling all space, and the interstices of all material objects. This medium is not light itself, but it is susceptible of being thrown into the vibrations which constitute light; the undulations which fall upon the eye are converged by the lenses on to the retina producing the sensation of light. Upon this theory, therefore, the phenomena are explicable upon a mechanism similar to that by which the vibrations of elastic media are known to be propagated; such, for example, as that by which the undulations of the atmosphere are conveyed to the ear and excite the sensation of sound. The ether by means of which light is supposed to be transmitted, though possessed of inertia, is not admitted, like the atmosphere, to be affected to any sensible extent by gravity.

At present the theory of undulation is universally adopted, as it affords the most complete explanation of the facts upon which the science of optics is based. The analogies between light and sound are not the least striking and interesting amongst the proofs adduced in its support. Indeed, it will greatly facilitate the comprehension of the mechanism by which light is supposed to be propagated, if we first examine some of the phenomena of sound which admit of being traced in a manner more directly appreciable to common apprehension than that of light.

(91) *Illustrations of Undulations from the Phenomena of Sound.*—We have abundant evidence of the fact that sound, whenever produced, arises from a series of vibrations which are occasioned by any sudden impulse, such as a blow, communicated to any substance possessed of even a very small elasticity. In other words, the impression which we receive is due to the vibration into which the particles of the sounding body are thrown; these vibrations react upon an elastic medium, such as the air: the impulses are communicated by the motions of the particles of air to the ear, and by reaction upon the auditory nerves they excite the sense of hearing.

These motions of sounding bodies are frequently not too rapid to be traced by the eye; for example, a stretched string whilst sounding may be easily seen to be in rapid vibration. Again, if a goblet be dusted over with a little sand, or any

fine powder, and a violin bow be drawn across its edge so as to elicit a sound, the particles of dust will be briskly agitated. And in the common experiment of half filling a finger-glass with water, and producing a sound by drawing the moistened finger along its edge, the water within, whilst the sound lasts, is beautifully rippled, to an extent corresponding with the loudness of the tone. These motions are also distinctly visible in the prongs of a tuning-fork whilst it is in the act of producing sound (fig. 66). Such vibrations, however, to render them audible, require the intervention of an elastic medium to convey them to the ear. If a bell be suspended in the receiver of the air-pump, and struck, it will be distinctly heard whilst the vessel is full of air; but, as the exhaustion proceeds, on repeating the stroke it will gradually become feebler, and at last will be inaudible, or nearly so.

FIG. 66.

Other media besides air may, however, be employed for the transmission of sound. A bell may be rung, for instance, under water, and will be heard by a person also under the water at even a greater distance than in the air. Wood will likewise transmit sound freely, and to still greater distances than atmospheric air.

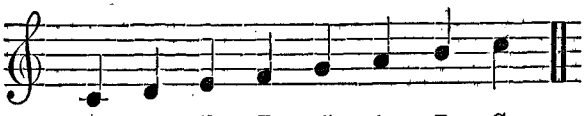
These impulses require time for their propagation, and the rate of propagation varies in different bodies. Sound travels, for example, at the rate of 1120 feet (341 metres) in a second through air at the temperature of 16° C., of 4708 feet (1435 metres) through water, and of 16,130 feet (4916 metres) per second through iron wire.

The intensity of sound, like that of all forces radiating from a centre, diminishes as the inverse square of the distance; and as it is propagated in waves or undulations, it is subject to reflection from obstacles interposed in its course, producing the various kinds and forms of echo.

(92) *Varieties of Sound.*—Sounds differ from each other in *loudness, quality,* and *pitch.* The *loudness* of a sound depends upon the extent of the vibration. A tuning-fork vibrating freely in the air produces only a feeble sound; but if the handle be placed upon a table whilst the prongs are vibrating, the wooden surface is thrown into powerful simultaneous vibration, and a loud sound is emitted. *Quality,* or *timbre,* depends on the form of the sounding body, and the nature of the material composing it. Differences such as are perceived between the same note when produced by a flute, a trumpet, or a violin, are due to this variety. Successive impulses following each other rapidly at irregular intervals, constitute a noise or continued sound, like the rumbling of carriages in the street, or the rattle of machinery; but when they follow at regular intervals, with a velocity exceeding 16 vibrations in a second, they produce a musical note. The *pitch* of the note depends on the frequency of these vibrations; the more rapid the vibrations, the sharper does the sound become. The connexion of pitch with the frequency of vibration may be readily verified by pressing a card against the edge of a toothed wheel, which is made to revolve slowly; the distinct strokes of the card against each tooth are heard at first; but by increasing the rapidity of rotation, a low humming note is given out, and as the velocity increases the sound becomes more acute.

Musical notes all have a fixed numerical relation to each other, each octave as the scale ascends having twice as many vibrations in equal intervals of time as the corresponding note of the octave immediately below it. The ratios are exhibited in the annexed table:—

Ratio of the Sounds of the Musical Scale.



C	D	E	F	G	A	B	C
1	$\frac{9}{8}$	$\frac{5}{4}$	$\frac{4}{3}$	$\frac{3}{2}$	$\frac{5}{3}$	$\frac{15}{8}$	2

	Vibrations per Second.	Intervals.
C	256	
D	288	32
E	320	32
F	$341\frac{1}{3}$	$21\frac{1}{3}$
G	384	$42\frac{2}{3}$
A	$426\frac{2}{3}$	$42\frac{2}{3}$
B	480	$53\frac{1}{3}$
C	512	32

In this table, a tuning-fork is considered to have made one complete *vibration* whilst the prong is passing from *a* to *b* and back again (fig. 65) : the motion from *a* to *b* or from *b* to *a* is called an *oscillation*. The further consideration of this subject would, however, be irrelevant in a work on chemistry, as it belongs to the physical science of acoustics.

It rarely happens that all the particles of a sounding body are simultaneously vibrating. A sounding body generally divides itself into portions vibrating in opposite directions; the intermediate lines or points are quiescent, and these quiescent portions are termed *nodal* lines or points. If a flat plate of glass be held horizontally by the point of the finger and thumb near its centre, and its surface be sprinkled with sand, on eliciting a musical note by drawing a violin bow across its edge, the sand will accumulate on the stationary parts, and show clearly the position of the nodal lines. By altering the points at which the glass is held, the nodal lines, and the note elicited, may be made to undergo a variety of interesting changes.

The stress exerted by the accumulation of these minute molecular motions is extraordinary. A feat occasionally performed by a powerful singer is to crack a glass by swelling his voice upon the note to which the glass responds. Savart has made some important experiments in relation to this subject. (*Ann. Chim. Phys.* 1837 [2], lxv. 384.) He found that a copper band, 3 metres long, 7 or $8^{mm.}$ wide, and $1^{mm.}$ thick, to which 30 or 40 kilogrammes was attached, when made to vibrate longitudinally, became lengthened 15 or 20 centimetres. In the same way a cylinder of brass $1{\cdot}407^{m.}$ in length, and $34{\cdot}95^{mm.}$ in diameter, became lengthened during its longitudinal vibration to an extent that would have required the application of a tension equal to the weight of 1700 kilogrammes. It is needless to insist on the important practical bearing of these facts on the construction of metallic machinery liable to regular partial oscillation, however slight or apparently trivial such vibrations may be.

The experiments just detailed will show in what way it has been clearly ascertained that it is by successive regularly recurring motions, or undulations, that sound is propagated. A similar principle has been with great success applied, with certain modifications, to trace the yet more interesting and complicated phenomena exhibited by light.

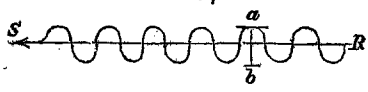
(93) *Mechanism of Undulation.*—There are two modes in which waves may be propagated: 1, in highly elastic media like

air the particles of the medium undergo alternate condensation and rarefaction in the *same* direction as that in which the motion is communicated, and in which the wave is travelling, as occurs in the passage of sound through air; 2, in other cases the motion is at *right angles* to that in which the wave is advancing.

A movement of the second kind takes place in water when a stone is dropped into it, or when its surface is ruffled by a breeze. Though the motion is propagated from the point struck, towards the edges, in circles continually widening, the particles of the liquid do not themselves travel onwards from the centre towards the circumference, but are alternately elevated and depressed, as may be seen by watching the movements of a cork or other light floating object; each vertical line in succession receiving and transmitting the motion produced by the first impulse, which gradually diminishes in intensity as the squares of the distance increase, and as the circle becomes more extended.

The mode in which the undulations of light are believed to be transmitted may be illustrated by loosely stretching a long cord, and striking it from above downwards near one end: the motion will be propagated in a vertical plane in successive waves from one extremity to the other, each portion of the cord becoming alternately first higher and then lower than the position which it assumes when at rest. If the cord be struck laterally, the waves will occur from side to side in a horizontal plane. In the passage of a ray of light, the motions of the particles of ether interposed between the eye and the luminous object will, like those of the cord, be at right angles to the track of the ray, or to that line in which the wave is advancing, and in the same plane as that in which the impulse was given. Let R S (fig. 67) be the direction of the ray, the motion of the particles of the ether will be in the direction *a b*, at right angles to the course of the ray. The length of the line *a b* is called the amplitude of the vibration; and the distance from one crest of a wave to the next the wave-length.

FIG. 67.



That the undulations which produce light are occasioned by motions of the particles of the ether at right angles to the track of the ray may be inferred from the phenomena of polarization:—In polarized light, as will be seen more fully hereafter, the results are such as can be explained only by admitting that ordinary light is resolved into two sets of rays, the undulations of which

occur *in planes at right angles to each other*, although the two sets of rays travel onwards in the same direction.

If light were propagated by waves of alternate condensation and refraction, such waves from their nature could not be referred to any particular plane, and the phenomena of polarization consequently could not exist.

(94) *Transparency and Opacity.*—Bodies through which light passes freely, such as glass or air, are termed *transparent*, or *diaphanous* (from διὰ, through, φαίνω, to appear); they allow objects to be seen distinctly through them, whilst the majority of substances which, like wood, metals, &c., do not allow its passage, are said to be *opaque*. No substance, however, is perfectly transparent. The purest air arrests a portion of light: Young adopts the estimate that the horizontal sunbeams, which pass through about 200 miles of atmospheric air before they reach the eye, possess only one two-thousandth of their original intensity; and he states that a column of water 7 feet in depth, has been found to arrest one-half of the light which enters it. On the other hand, there is no such thing as perfect opacity. Gold, one of the densest of the metals, may be hammered out into very thin leaves, which transmit a green light if the metal be pure, and a purplish light if it be alloyed with silver. Between the extremes of opacity and transparency are innumerable gradations. Bodies vary greatly in *translucency*, that is, in their power of transmitting light. Porcelain is a translucent body; it breaks up the rays, but transmits a softened light, though it does not allow the form of an object to be seen if the porcelain be interposed between that object and the eye.

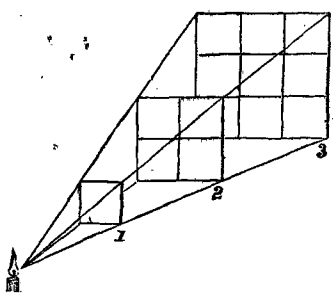
Light proceeds through all homogeneous transparent media in straight lines from the object; these lines diverge or radiate in all directions from a luminous point, and a *ray* of light is an indefinitely narrow portion of a stream of light. The path of the rays in a direct line may often be traced across a darkened room into which a sunbeam is admitted, by the floating particles of dust, which reflect a small portion of the light in different parts of its course into the eye of the observer. The mere passage of light through a transparent object does not excite the sense of vision, neither can the eye track the direction of the ray, unless the vibrations be carried towards the observer by reflection from the surface of some material object.

The impression of light upon the retina lasts for a brief interval, varying in different persons from a tenth to an eighth of

a second, after the light itself has ceased, and gives rise to many curious effects: for instance, the act of blinking produces no impediment to correct vision; a bright point made to revolve rapidly in the dark is seen as a luminous circle, and the jets of flame which in fireworks are whirled round before the eyes of the spectators, assume the form of wheels or stars of fire.

(95) *Law of Diminution of Light by Distance.*—When light diverges from a luminous centre, its intensity diminishes, like that of all radiations, not inversely as the distance, but inversely as the square of the distance. A little consideration will render the reason for this obvious:—Suppose the flame of a candle, or any luminous point, to be placed in the centre of a hollow sphere 2 metres in diameter, its light will fall upon the whole internal surface of the sphere, and the candle will be 1 metre distant from each point: a square centimetre of that surface will receive a given amount of light. The same candle, if placed in the middle of a globe 4 metres in diameter, will be at 2 metres distance from each point of the surface, or at double the distance that it was in the first globe, but its light will still illuminate the whole of the interior. The surface of the second globe, however, is four times greater than that of the first, because the surfaces of spheres are to each other as the squares of their radii; in this case as $1^2 : 2^2$, or as 1 to 4; consequently each point, or each square centimetre, of the surface of the larger sphere, will receive only one-fourth of the light that fell on an equal space in the smaller globe, and yet the candle is only twice as far from it: so, if the globe were 8 metres across, the distance of the candle being now 4 times as great as in the first globe, the surface to be illuminated is 16 times as large, and consequently, a square centimetre of the 8-metre globe would receive only $\frac{1}{16}$ of the light that fell on a square centimetre of the 2-metre globe. A board at 1 metre from a candle receives a certain amount of light, at 2 metres it receives $\frac{1}{4}$ of that amount, at 3 metres $\frac{1}{9}$, at 4 metres $\frac{1}{16}$: and experiment shows that a board, 1 decimetre square, at 1 metre distance, would cast a shadow that would cover a board exposing 4 times the surface, or 2 decimetres in the side, if placed at a distance of 2 metres, as shown in fig. 68.

FIG. 68.



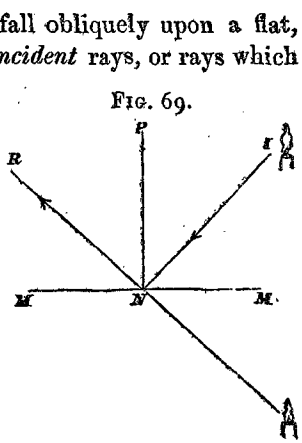
(96) *Photometry.*—An application of this law affords a ready means of approximately determining the relative intensities of two lights which do not

differ greatly in colour. Suppose, for instance, it were necessary to ascertain the illuminating power of a gas-light burning 5 cubic feet (or 142 litres) of gas per hour, as compared with that of a sperm candle burning 120 grs. (or 7·775 grms.) of spermaceti per hour:—Place at the distance, say of 100 inches from the gas-light, a vertical screen of white paper, and in front of this, at an inch distance, a narrow strip of wood or of metal, so as to cast a definite shadow. Between the gas-light and the screen place the candle, at such a distance that the shadow of the same object cast by the candle upon the screen shall have as nearly as possible the same intensity as that produced by the gas. Say that the distance of the candle from the screen is 27·75 inches. The shadow from each light is illuminated by the rays proceeding from the other light. If the shadows be sensibly equal, the amount of light falling upon the screen from each source must at that distance be equal also: the relative intensities of the two lights are then found by squaring the distances of each light from the screen; the gas-light will consequently cast a light which bears the same ratio to that of the candle as $100^2 : 27{\cdot}75^2$; or as 12·986 to 1.

When light falls upon any object it may be disposed of in three different ways. 1st, it may either be bent back or *reflected;* 2nd, it may be allowed to pass on in an altered direction, that is, it may be *transmitted* and *refracted;* or 3rd, it may disappear altogether, and be *absorbed.*

(97) *Reflection.*—If a ray of light fall obliquely upon a flat, polished surface, a large portion of the *incident* rays, or rays which fall upon the surface, is reflected or thrown off obliquely, at an angle formed on the other side of a perpendicular to the point of incidence, equal to that formed between the incident ray and the perpendicular. Fig. 69 is intended to illustrate the law of reflection. If in this figure, I N represent the incident ray, M M the mirror, P N a perpendicular to the mirror at the point of incidence, P N I will be the angle of incidence, N R the reflected ray, and P N R the angle of reflection formed between the same perpendicular and the reflected ray.

Fig. 69.



The law which regulates the reflection of light is expressed by saying that 'the angle of reflection is equal to the angle of incidence': the incidence and the reflected ray are always in the same plane, and that plane is perpendicular to the reflecting surface. When the incident ray is perpendicular to the surface, the reflected ray is therefore also perpendicular, and coincides with the incident ray, but it does so in no other position.

In fig. 69, the angle of reflection, P N R, is equal to the angle of incidence, P N I, but they are on opposite sides of the perpen-

dicular. An eye at R looking into the mirror, would see the candle behind the mirror, and at the same distance behind it as the candle flame is in front. An object always appears to lie in the direction of the line which the ray last traversed when it reaches the eye.

The power of reflecting light varies very greatly in different bodies. In some, as in the metals, reflection is almost perfect; in others, as in charcoal, or in black velvet, it is almost wanting; but whenever light passes out of one *medium* or transparent body into another, no matter how perfect the transparency of such media may be, reflection more or less complete takes place at their common surface, and the greater the difference in refractive power of the two media, the more complete is the reflection.

Except in the case of the metals, in which reflection is most complete at the smaller angle of incidence, it is found that the greater the angle of incidence the more complete is the reflection; so that the surface of a smooth body, such as plaster of Paris, or hot-pressed writing-paper, may thus afford a tolerably perfect image of a luminous object, if the reflection be effected under a great angle.

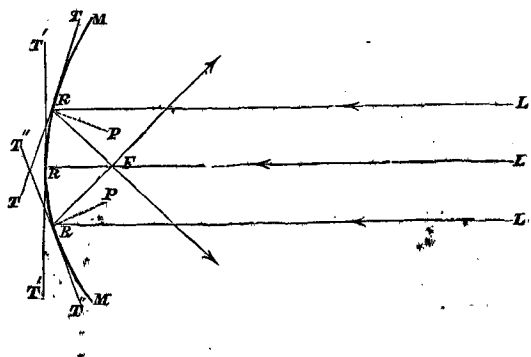
Bodies in general do not possess surfaces actually flat; to common observation they may be flat, but when optically examined, their surface is found to consist of an indefinite number of minute planes inclined to each other at all possible angles, and therefore receiving and reflecting light in all possible directions. When by the operation of polishing they are so much reduced as not to be elevated or depressed more than about the millionth of an inch, they appear to become incapable of acting separately, and produce the effect of a uniform surface. (Young.) If a beam of light admitted into a dark room fall upon a bright metallic surface, a brilliant spot of light will be perceived in one particular position, the direction of which can be varied by altering the inclination of the mirror to the ray, but the mirror will be nearly invisible in all other directions, and the room will remain dark; but if for the mirror a sheet of white paper be substituted, the paper will be visible in every direction almost equally, and a general though slight illumination of the apartment will be perceived. It is this irregular reflection or *scattering* of the light in all directions, which renders non-luminous objects distinguishable in the light. The light of the moon and of the planetary bodies furnish instances of this kind. A further evidence of the value of this scattering or secondary radiation, is afforded by the difference between the mild and softened light which is reflected from the heavens when par-

tially covered with clouds, and the strong lights which fatigue the eyesight in a cloudless summer's day. It is entirely to this secondary radiation that we owe the generally diffused and subdued light of day, even when the sun itself may be concealed by clouds; and the morning and evening twilight, while the great luminary itself is below the horizon, is due to the same cause, each illuminated particle of the atmosphere contributing its share in producing this effect.

(98) *Reflection from Curved Surfaces.*—When light is received upon a regular curved surface, it undergoes reflection according to the usual law, the reflection from each point of the curved surface being, in fact, the same as from a plane, tangent to the curve at the point of incidence. If, therefore, the form of a parabolic concavity be given to a mirror, and light in parallel rays be allowed to fall upon its surface, all the reflected rays will be directed towards a point at which they will cross each other, and continue their progress as before, the upper ray now becoming undermost, and *vice versâ*. This point of intersection is called the *focus* of the mirror.

Let M M, fig. 70, represent the section of the curved surface; each of the rays L R, L R, will be reflected from it as from planes T T, T′ T′, T″ T″, tangent to the curve at the points of incidence of the respective rays; they will consequently meet at the focus F, cross there, and subsequently diverge. P R, P R represent the lines perpendicular to the tangents.

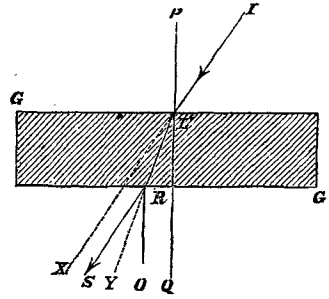
FIG. 70.



(99) *Simple Refraction.*—When a ray of light falls upon the surface of an uncrystallized transparent substance of uniform density, one portion of the light is regularly reflected, and another portion is scattered, by which the surface is rendered visible, whilst a third portion is transmitted. We will now confine our attention to that portion of the light which is transmitted. If the ray be incident upon the surface of the body in a perpendicular direction, it continues its course unchanged; but if it fall upon the surface obliquely, its direction is suddenly altered as it

enters the transparent medium; it then passes on in its new direction in a straight line, and on quitting the medium it is again abruptly bent back and rendered parallel to its original course, provided that the surface of entrance and the surface of exit be parallel to each other. This change in the course of the ray is termed *refraction*. If, in fig. 71, G G represent a section of a plate of glass with parallel sides, a ray of light, I L, incident obliquely upon it, does not pass straight on in the direction L X, but is deflected to L R, towards the perpendicular, P Q; on quitting the medium at R, it is again bent out of its new direction, L Y, towards S, but this time the refraction is from the perpendicular, R O, and the ray, R S, becomes parallel to its original course, I X. On passing from a medium like air, into another like glass, the ray is bent towards a line perpendicular to the common surface of the two media; on again passing out from glass into air; or from a more refracting to a less refracting medium, it is bent from the perpendicular to the same amount. The cause of refraction is the diminution of velocity with which light passes through more powerfully refracting bodies (113).

Fig. 71.



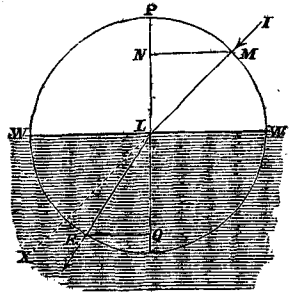
Different media vary greatly in refracting power; combustible bodies in general having the highest refracting energy. It was upon this general observation that Newton founded his conjecture that diamond was 'probably an unctuous substance coagulated'; the combustibility of the diamond has been since fully verified.

(100) *Law of Refraction.*—The more obliquely the light falls upon the surface of the refracting body the greater is the amount of refraction which the ray experiences. The extent of the refraction, therefore, varies with the angle of incidence, but by a knowledge of the following law it may easily be calculated for all angles in any given substance, if its amount for any one angle has been carefully determined for that particular substance. This law of refraction may be expressed by stating that when light passes from one medium into another, 'for the same two media, the sines of the angles of refraction and of incidence always bear the same ratio to each other.' The quotient obtained by dividing the sine of the angle of incidence *in vacuo* by the sine of the angle of refraction in any medium, expresses the *index of*

refraction of that medium. The incident and the refracted ray are always on opposite sides of a line drawn perpendicular to the common surface of the two media, but they always lie in the same plane, and this plane is perpendicular to the surface of the refracting medium.

Fig. 72 may assist in explaining this important law. Let W W represent a section of the refracting medium, I L the incident ray, and L R the refracted one. Let P L Q be the perpendicular to the refracting surface, passing through the point of incidence, L. With any radius, L R, describe from the centre, L, the circle, R M P; from M and R let fall the perpendiculars M N and R Q, on P Q; M N will then represent the sine of the angle of incidence, I L P, and R Q the sine of the angle of refraction, R L Q; and $\frac{MN}{RQ}$ gives the index of refraction, which is uniformly the same for the same substance, whatever be the angle of incidence. In the diamond, for instance, M N is always 2½ times as long as R Q; in water it is 1⅓ times the length of R Q.

FIG. 72.



The following table contains the *indices of refraction* of a few substances; the light being supposed to pass from atmospheric air:—

Diamond	2·439	Oil of Vitriol	1·434
Phosphorus	2·224	Alcohol	1·372
Carbonic Disulphide ...	1·678	Ether	1·358
Rock Salt	1·557	Water	1·335
Quartz	1·548	Ice	1·308
Castor Oil	1·490	Tabasheer	1·111

The examination of the refracting power of bodies in their gaseous, or least complex molecular condition, possesses a special interest; the subject was first investigated by Biot and Arago, and it was carried further by Dulong. (*Ann. Chim. Phys.* 1826 [2], xxxi. 154.)

It appears that there is no simple relation between the refracting power of gases and their densities. The vapour of hydrochloric ether, for example, differs but little in density from sulphurous anhydride, though the refracting power of the former body is nearly two-thirds greater than that of the latter: and ordinary ether has more than double the refracting power of chlorine, though their densities in the aëriform state are nearly the same.

The refracting power of a gas or of a vapour is proportioned to the pressure, and is not affected by temperature, at least so far as experiments on pressures not greater than that of one atmosphere, and on temperatures ranging between 7° and 38° C. can decide the question. The refracting power of a mixture of gases is equal to the sum of that of its constituents calculated for the pressure of each constituent in proportion to the amount present in the mixture. But the refracting power of a compound may be either greater or less than that of the sum of its constituents.

More recently Le Roux (*Ann. Chim. Phys.* 1861 [3], lxi. 385) has extended

those observations to the vapours of certain simple substances which can only be volatilized at elevated temperatures. He found the refringent energy ($\frac{\mu^2-1}{d}$, μ being the index of refraction and d the vapour density) of sulphur vapour to agree with that of oxygen as determined by Dulong, and that of the vapour of phosphorus agreed closely with a similar determination for nitrogen. It is possible that these coincidents are only accidental, for elements which are analogous in their chemical relations have not been found to exhibit generally any close agreement in refracting power.

Le Roux remarks that in the case of gaseous bodies it is a matter of indifference whether the refringent energy be calculated from the formula $\frac{\mu-1}{d}$ or $\frac{\mu^2-1}{d}$; since the index of refraction μ is of the form $1+\epsilon$, ϵ being a very small quantity; consequently its square will be equal to $1+2\epsilon$ within a quantity certainly less than that due to errors of observation.

The following table exhibits the principal results of the experiments of Dulong, the four last being due to Le Roux. The refracting power of each gas as compared with air is calculated upon the supposition that they are all under a pressure of $760^{mm.}$ at 0° C.

Name of Substance.	Observed Density.*	Refracting Power.			Index of Refraction $=\mu$.
		Air. $=1{\cdot}0$.	Absolute $=\mu^2-1$.	$\frac{(\mu^2-1)\times 1000}{\text{Density.}}$	
Air	1·0000	1·000	0·000588	0·588	1·000294
Oxygen	1·1026	0·925	0·000544	0·493	1·000272
Hydrogen	0·0685	0·469	0·000276	4·029	1·000138
Nitrogen	0·976	1·020	0·000600	0·615	1·000300
Chlorine	2·47	2·627	0·001545	0·625	1.000772
Nitrous Oxide	1·527	1·711	0·001006	0·659	1·000503
Nitric Oxide	1·039	1·031	0·000606	0·583	1·000303
Hydrochloric Acid ...	1·254	1·527	0·000898	0·716	1·000449
Carbonic Oxide	0·972	1·157	0·000680	0·684	1·000340
Carbonic Anhydride ...	1·524	1·527	0·000898	0·589	1·000449
Cyanogen	1·818	2·837	0·001668	0·917	1·000834
Olefiant Gas	0·980	2·306	0·001356	1·384	1·000678
Marsh Gas	0·559	1·507	0·000886	1·585	1·000443
Ethyl Chloride	2·234	3·726	0·002191	0·981	1·001095
Hydrocyanic Acid... ...	0·944	1·534	0·000902	0·955	1·000451
Ammonia	0·591	1·309	0·000770	1·303	1·000385
Phosgene Gas	3·442	3·944	0·002319	0·674	1·001159
Sulphuretted Hydrogen	1·178	2·190	0·001288	1·093	1·000644
Sulphurous Anhydride ...	2·247	2·262	0·001330	0·592	1·000665
Ether	2·580	5·207	0·003062	1·187	1·001530
Carbonic Disulphide ...	2·644	5·105	0·003002	1·060	1·001500
Phosphuretted Hydrogen	1·256	2·685	0·001579	1·257	1·000789
Sulphur	6·617		0·003261	0·493	1·001629
Phosphorus	4·355		0·002730	0·627	1·001364
Arsenic	10·39		0·002229	0·214	1·001114
Mercury	6·976		0·001112	0·159	1·000556

Many familiar phenomena receive an easy explanation from the law of refraction. If a coin be placed in an opaque vessel, and the observer retire until the edge of the basin just hides it from his view, the coin will again become visible if water be carefully

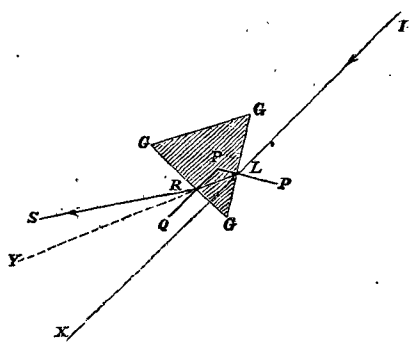
* These densities have since in many cases received corrections.

poured in without disturbing its position; the rays of light proceeding from the coin, which before passed above the eye of the observer, are now abruptly bent downwards from the perpendicular, as they emerge into the air, and the image of the object is conveyed to the eye. The coin appears to be raised, but never displaced to the right or to the left of its true position; the refracted ray, notwithstanding its change of medium, continues in the same plane, which is vertical to that forming the common surface of the refracting media. For a similar reason a straight stick plunged obliquely into water appears to be bent upwards abruptly, where it enters the liquid.

(101) *Refraction at Inclined Surfaces.*—Since the refraction is exercised at the surface of junction between the two media, and is governed by the inclination of the ray to a perpendicular to that surface, it is manifest that by altering the inclination of the surface at which the ray passes out of the medium, the inclination of the emerging ray may be altered; so that, instead of continuing its passage in a direction parallel to the one which it possessed on entrance, it may be made to deviate permanently from this to a greater or less extent.

If G G G (fig. 73) represent the section of a triangular *prism*, or bar of glass, the incident ray, I L, on entering this medium is bent towards the perpendicular, P P: on quitting it at R, it is bent from the perpendicular, Q P, and assumes a course, R S, permanently deflected from its new direction, L Y, and from its original direction, I X. This deflection is always towards the thick part of the prism. By employing two such prisms set base to base, the rays may be refracted towards one common line, where they would cross and diverge; and by using a lens of glass (fig. 74), with two convex surfaces, which are segments of spheres, the incident rays R L, R L, may be caused to converge towards a common focus F; each portion of the curved surface refracting the ray in the manner of a plane, T T, T′ T′, T″ T″, tangent to the curve at that particular spot or point of incidence.

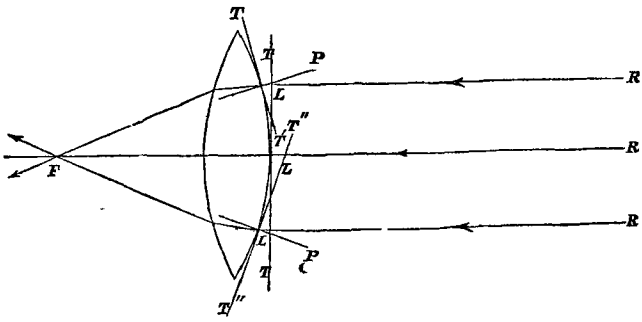
FIG. 73.



(102) *Total Reflection.*—In the passage of light from a more

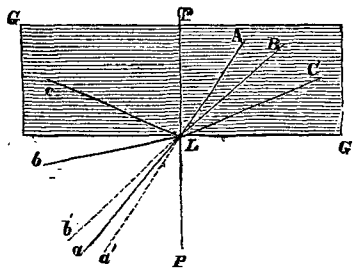
into a less powerfully refracting medium, as when light passes from glass into air, the obliquity of the refracted ray increases as the

FIG. 74.



angle of incidence increases, until at length the refracted ray becomes parallel to the common surface of the two media. Light, which traverses the more refracting medium and becomes incident upon this common surface at an angle more oblique than this, ceases to be refracted; refraction becomes impossible, and the ray is wholly reflected within the medium. The angle of incidence at which this phenomenon first shows itself is termed the *angle of total reflection*. In fig. 75, let G G represent a plate of glass with parallel sides, P L P a perpendicular at the point of incidence. The incident ray, A L, instead of passing to *a'*, would be refracted from the perpendicular P P to L *a* on emerging into the air; B L would be still more refracted from L *b'*, and the refracted portion L *b* would be nearly parallel with the surface of the glass, whilst C L would be incapable of refraction at all, and would be wholly reflected, as to L *c*. This phenomenon is easily seen by placing the back to the light and holding a glass of water a little above the level of the eye; on looking obliquely up through the water, a spoon, or other object placed in the glass, will appear to be perfectly reflected upon the surface where the liquid and the air meet. The same thing is seen by holding a glass prism horizontally before a window, and turning it slowly round while the observer faces the window; on looking down into the prism, the internal surface of each face in succession, as it becomes uppermost, reflects the lightwith the brilliancy of a mirror.

FIG. 75.



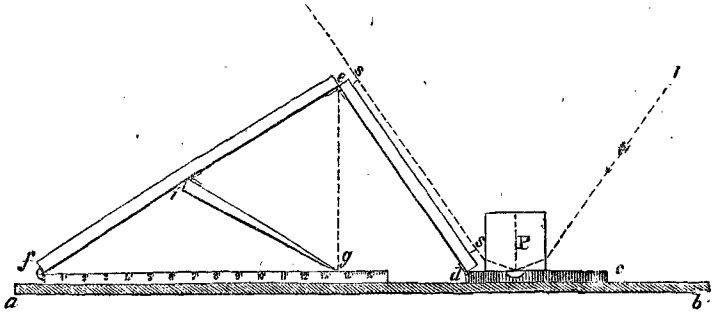
The diamond is indebted for much of its brilliancy to this total reflection, because owing to the high refractive index of this gem, total reflection commences at small angles of incidence.

(103) *Measurement of the Index of Refraction.*—The determination of the refractive index of a body is often a valuable guide in estimating its chemical purity. The adulteration of essential oils may thus be often detected with ease, when it would otherwise be difficult to ascertain it.

Wollaston contrived a simple means of determining the refractive index of a body in air, dependent upon the measurement of the angle at which total reflection commences. If this angle be measured in a glass prism, we are furnished with the means of determining the refractive index of the prism in air. Say that the angle C L P (fig. 75), at which total reflection of the incident ray commences in the prism, is found to be 39° 10′; the refractive index of the prism in air is calculated by dividing the sine of the angle of refraction by the sine of this angle of incidence: but the angle of *refraction* at which total reflection *begins* is always 90°; the refractive index therefore is $\frac{\text{Sine } 90°}{\text{Sine } 39° 10'}$ or $\frac{1 \cdot 0 0 0}{0 \cdot 6 3 1} = 1 \cdot 583$. Now cause a drop of any liquid to adhere to the under surface of the prism; provided that the refractive index of the liquid be less than that of the glass, the angle of total reflection will be increased: suppose the prism be moistened with water, the angle of total reflection will now be $57\frac{1}{2}°$. The water has a higher refractive index than air, consequently, the difference in refractive index between glass and water being less than that between glass and air, the angle of incidence required to produce total reflection is greater. The refractive index of the substance under trial may be ascertained by dividing the sine of its angle of total reflection, under these circumstances, by the sine of the same angle for the glass prism. In the case of water the refractive index is $\frac{\text{Sine } 57° 30'}{\text{Sine } 39° 10'}$ or $\frac{0 \cdot 8 4 3 4}{0 \cdot 6 3 1 5} = 1 \cdot 336$. The refractive index of solids with flat surfaces may be determined in the same way, by cementing them to the surface of the prism with some material of higher refracting power than the glass, such as balsam of tolu.

Wollaston's instrument, fig. 76, gives at once the refractive index sought without any calculation.

FIG. 76.



On a board, *a b*, is fixed a flat piece of deal, *c d*, to which by a hinge at *d*, is jointed a second piece, *d e*, 10 inches long, carrying two plane sights, *s* and *s*, at its extremities; at *e* is a second hinge connecting it with *e f*, which, if the prism employed has, as supposed, a refractive index of 1·583, must be 15·83 inches long; at the other extremity of *e f*, is a third hinge by which *f g* is connected with it; at *i* also is a hinge uniting the rod *i g*, which is half the length of *e f*, to the middle of *e f*; and then, since *g* moves in a semicircle, a line

joining *e* and *g* would be perpendicular to *f g*. The piece *c d* has a cavity in the middle of it, so that, when any substance is applied to the under surface of the rectangular glass prism, P, the prism may continue to rest horizontally on its extremities. When *e d* has been so elevated that the yellow rays in the fringe of colours, observable where total reflection terminates, are seen through the sights, the point *g*, by means of a vernier which it carries, shows upon the rule *f*, *g*, which is graduated to fractions of an inch, the number of inches and fractions of an inch which, when divided by 10, gives the refractive index sought. The length of the pieces *e f* and *d e*, are proportional to the refractive indices of the prism and of air. If the dotted line at P be a perpendicular to the reflecting surface, *l* P will represent the incident ray. (*Phil. Trans.* 1802, 365.)

Wollaston mentions that genuine oil of cloves had a refractive index of 1·535, but that some of inferior quality, which had probably been adulterated, had a refractive index of only 1·498.

The following table contains some of the results obtained by Wollaston with this instrument:—

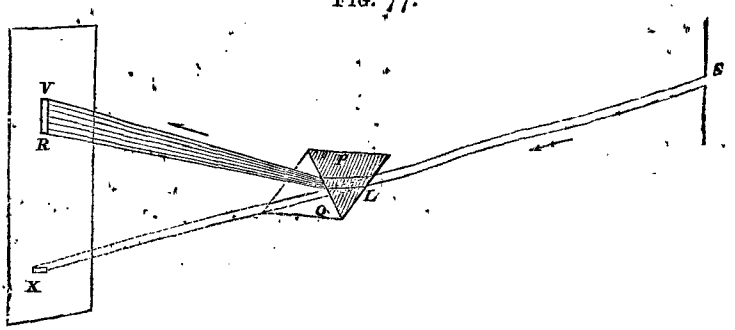
Refractive Index of Flint Glass Prism, P = 1·583.

Oil of Sassafras	1·536	Oil of Turpentin ...	1·476
Oil of Cloves	1·535	Rectified ditto	1·470
Canada Balsam	1·528	Oil of Olives	1·469
Capivi Balsam	1·507	„ Peppermint ...	1·468
Oil of Amber	1·505	„ Lavender	1·467
„ Nutmeg	1·497	Melted Spermaceti ...	1·446
„ Linseed	1·485	Sulphuric Acid	1·435
„ Lemons	1·476		

Professor Clifton and Mr. Sorby have independently devised a method of determining the refractive index of transparent bodies by placing them in the microscope, and measuring their thickness by the amount of movement of the microscope tube necessary to bring, firstly, the top of the fragment, and, secondly, the glass slide on which they stand, into focus; and subsequently observing the motion necessary to bring into focus a mark on the slide which is seen through the crystal. From these data the refractive index can be determined with accuracy; and the method can be employed with great advantage in recognizing small fragments of minerals.

(104) *Prismatic Analysis.*—Upon examining light that has undergone refraction by a prism, it is found that mere change in direction is only one of the phenomena observable. Suppose a beam of light, as represented at s L, fig. 77, be admitted through

Fig. 77.



a small slit, S, into a darkened room, and be there received upon a prism, P; if the light, after transmission through the prism, be allowed to fall upon a white screen, V R X, placed at a distance of three or four metres,—instead of a narrow slit of white light, X, corresponding to the aperture, an elongated coloured image of the slit is seen, as at V R, terminated by parallel ends, and exhibiting the hues of the rainbow. This elongation occurs in the plane of the reflected and refracted rays. Such a coloured image is termed the *prismatic spectrum*.

Newton, who first carefully investigated this remarkable fact, distinguished seven different colours, which gradually shade off one into the other,—viz., violet, indigo, blue, green, yellow, orange, and red. White light may therefore be regarded as the result of a mixture of rays of different colours, which are unequally acted upon by the prism. Each colour has its own peculiar refrangibility; the red, which deviates the least from its original course, is least refrangible, and the violet the most so; whilst the intermediate colours possess intermediate degrees of refrangibility. Having once been separated by refraction, no second refraction is capable of further decomposing any of these colours. They may, however, be recombined by using a second prism, in an inverted position (as shown by the dotted lines at Q, fig. 77), or by employing, what amounts to the same thing, a convex lens, in which case white light is reproduced at the focus of the lens. The composition of white light may be illustrated by dividing a circular disk of paper into seven sectors, each of an extent corresponding with the extent of the colour in the spectrum, and painting each with its appropriate colour; on causing the disk to rotate rapidly upon an axis passing vertically through its centre, the seven impressions will be given simultaneously to each point of the retina, and the paper will appear to be of a greyish white. The impossibility of obtaining pigments of the exact hue, or of the brilliancy of the coloured light of the spectrum, renders a pure white unattainable by this means.

The following is an elegant mode of showing the recomposition of white light from the colours of the spectrum. A prism is mounted so as to permit of a movement on its axis through a small arc, the spectrum is thus made to travel on a screen in the direction of its length. On moving the prism slowly, the colours are visible; but when the prism is made to oscillate very rapidly the colours are blended together, producing a streak of white light with a red border at one end and a blue at the other.

(105) *Theory of Colours.*—Upon this decomposibility of white

light, Newton founded his explanation of the colours of natural objects :—The objects are themselves devoid of colour, but when placed in white light they absorb the rays of one or more colours, and reflect the rest : the object, therefore, appears to be of the colour that would be produced by the ray or mixture of rays which it reflects ; green objects, for example, absorb the red rays and reflect the yellow and the blue ; purple absorb the yellow, and reflect the red and the blue. The rays thus absorbed are said to be *complementary* to those that are reflected ; a complementary colour being always that tint which when added to the primary colour upon the eye would constitute white light. This theory of colours may be illustrated by placing any coloured objects in light of one tint, or *homogeneous light*, as it is called, such as that of an isolated portion of the spectrum. A purple object, for instance, when placed in the blue rays will appear to be blue : if placed in the red rays it will appear to be red ; and a white screen, which has the power of reflecting all the colours, will take any tint in succession, according to the colour of the incident ray. An object of a pure red, on the contrary, will appear to be black in any but the red ray, because it absorbs all the other colours as perfectly as charcoal or black velvet absorbs white light or rays of all colours.

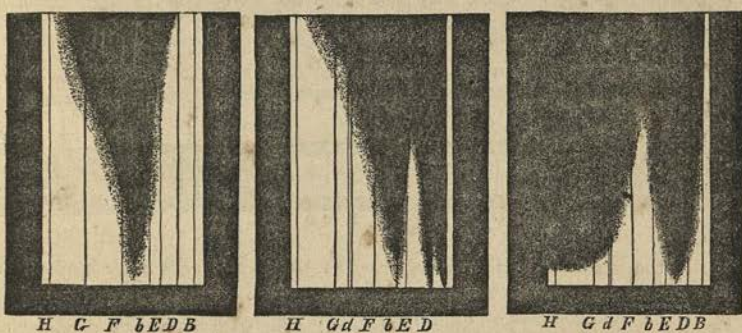
Hence it appears that white light may be decomposed by absorption, as well as by refraction or prismatic analysis. By transmitting white light through transparent coloured media, we may obtain rays of any given tint : the light thus obtained is not always the same as that produced by prismatic analysis, though apparently of the same colour ; by transmission through a coloured medium, a green, for instance, may be obtained, which may either be identical with the green isolated by the prism, and then it cannot further be separated into its components ; or it may be a compound colour resulting from the intermixture of rays of different degrees of refrangibility, and in this case it is susceptible of further decomposition. The coloured light that is obtained by absorption is seldom so pure as that furnished by prismatic decomposition.

Gladstone (*Q. J. Chem. Soc.* 1856, x. 79) has made some interesting observations upon the relation existing between the chemical composition of a body and the absorbent effect which it exerts upon transmitted light. His experiments were performed upon substances in solution which were placed in a wedge-shaped vessel or hollow prism, with the view of ascertaining the influence of different thicknesses of liquid upon the incident light. A beam of diffused light was admitted through a vertical slit into a darkened chamber, and the line of light thus obtained was allowed to fall upon the vessel held with the thin end of the wedge downwards, so that the light passed through different thicknesses of the solution, from the thinnest film to a stratum of an inch ($25^{mm.}$) in depth. The transmitted light

was then examined by means of a good prism. The light which passes through the thinner strata yields a spectrum generally differing but little from that of daylight; but that which has traversed greater depths of liquid exhibits a rapid disappearance of certain portions of the rays, whilst other rays are but little affected. Fig. 78, 1, shows the spectrum obtained by transmitting a beam of daylight through a dilute solution of a salt of cobalt, which appears to be of a delicate rose colour to the unaided eye. The same salt in more concentrated solutions appears to be of a rich blue, and exhibits a spectrum shown at fig. 78, 2, which represents the appearance of the spectrum furnished by a strong solution of cobaltous chloride in alcohol. The letters correspond to those of Fraunhofer's lines (106), the right-hand side of the figures indicating the red end of the spectrum; the lower part of the figures showing the effect of the thinnest strata of liquid.

It was ascertained from an extensive series of observations made in this manner, that when the salts formed by the union of a coloured base with different colourless acids were examined, the compounds of the same base nearly always exhibited a similar absorbent action upon the spectrum. Even in *dichromic* media, or solutions which, under certain circumstances, appear to the unaided eye to transmit light of one tint, and, under certain other circumstances, to transmit light of a different tint, this law generally holds good. An exemplification of this fact is seen in the case of the chromic salts, some of which exhibit a green colour when in solution, others a red or purple hue. Now all these salts furnish a spectrum, the general form of which is shown in fig. 79, in which the indigo

FIG. 78. 1. FIG. 78. 2. FIG. 79.



and the green rays are soon cut off, whilst the red and bluish-green rays are comparatively little affected. By some salts, such as chromic acetate, the green rays are absorbed much more rapidly than the red, and hence these solutions have, even in thin layers, a red colour: others, as the chromic chloride, are green when their solutions are seen in thin layers, but look red or purple when viewed in considerable mass by transmitted light.

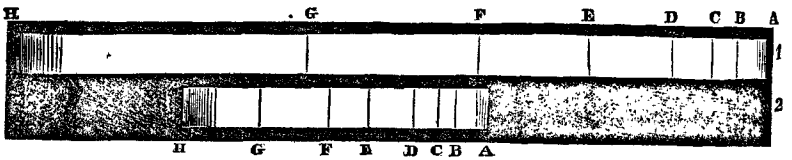
Some salts, even though their solutions have but little colour, furnish very characteristic spectra. This is particularly the case with solutions of didymium, which are of a feeble rose colour, but they exhibit two very black lines, one in the yellow, the other in the green. These lines are visible in the spectrum even when the solution is very dilute, and they may be employed to indicate the presence of small quantities of didymium in solutions of lanthanum and cerium, in which no such lines occur.

In artificial flames it is very generally the case that certain

colours are present in smaller proportion than others, and are even sometimes altogether wanting. Strontic nitrate, for instance, gives a red tint to burning bodies; and the prism shows that in such light the blue and violet, or more refrangible rays, are singularly deficient. Common salt produces in burning bodies a nearly pure and homogeneous yellow light, which may be used to illustrate the observations just made upon the cause of colour in natural objects. The brilliant colours of insects or of the plumage of birds, strike strangely on the eye when seen in this yellow light.

(105 *a*) *Dispersive Power.*—The prismatic analysis of white light, which has just been considered, is not due entirely to the refracting power of the body by which it is effected. Another element of great importance is the *dispersive* power, which is independent of refraction. Two substances may possess the same mean refractive index, in consequence of which the mean deviation of the rays transmitted will be the same, and yet the spectra which they furnish may be of very unequal lengths. If a hollow prism be made of plates of glass, and filled with oil of cassia, the spectrum which it produces will be more than double the length of that furnished by a similar prism of flint glass. The dispersive power of oil of cassia is much greater than that of flint glass, especially for the more refrangible rays from F to H, and hence there is a great difference in the length of the two spectra, though the mean refracting powers of the two media do not differ materially. The comparative lengths of these spectra, as obtained from prisms of equal angles, are given in fig. 80. No. 1 is the spectrum of oil of cassia; 2 that of flint glass.

FIG. 80.



In the construction of *achromatic* lenses, two media which differ in dispersive power are employed; by this means the fringe of colours, which is always perceptible around the margin of an object viewed by an ordinary lens of high magnifying power, is removed.

(105 *b*) *Sensitiveness to Heat.*—Gladstone and Dale have published (*Phil. Trans.* 1858, 887) the results of an inquiry into the influence of temperature upon the refracting and dispersive powers of bodies upon light. They find that the index of refraction diminishes in every substance as the temperature increases. The degree of this *sensitiveness* to the effect of heat varies much in different substances; melted phosphorus and carbonic disulphide being the most sensitive, and water the least sensitive of the bodies experimented on by them. This sensitiveness, however, is independent of the refracting or the dispersive power of the substance; ether, for example, being much more sensitive than water to the action of heat, though the refracting and the dispersive powers of the two liquids are nearly the same. Those bodies which expand most by heat are generally the most sensitive. No sudden change of sensitiveness has, however, been observed on the approach of the liquid to the boiling point. The length of the spectrum also decreases as the temperature rises, the effect of heat being most marked in those substances which have the highest dispersive power. The dis-

persive power is invariably diminished by rise of temperature, though not at the same rate as the refractive index, which is found to diminish in proportion as the density diminishes.

(105 *c*) *Influence of Chemical Composition on Refraction.*—Dale and Gladstone further found that the refractive index of any body, minus unity, divided by the density, gives nearly a constant quantity, which they term the *specific refractive energy* of the body. This result is confirmed by Landolt, who has made an extended series of experiments upon the influence of chemical composition upon refracting power. (*Pogg. Annal.* 1864, cxxii. 545, cxxiii. 595.) If μ_c be the refractive index of the line C, d the density of the compound, and P its molecular weight, the constant $\left(\frac{\mu_c - 1}{d}\right)$ would be what Landolt terms the *specific refractive energy*, and P $\left(\frac{\mu_c - 1}{d}\right)$ its *equivalent of refraction*. From his observations Landolt draws the following conclusions, which confirm and extend those of Gladstone and Dale:—

1. Metameric bodies have usually very nearly the same specific refractive energy, and consequently, the same equivalent of refraction. Gladstone and Dale, however, remark that though this is true where there is close chemical relationship, isomeric bodies are sometimes widely different in optical properties, as in the case of aniline and picoline.

2. In polymeric bodies the index of refraction and the density increase with each duplication of the formula, but the specific refractive energy diminishes slightly; the indices of refraction do not, therefore, increase exactly in multiple proportion.

3. In homologous series, with few exceptions, the index of refraction and the specific refractive energy increase as the terms ascend in the series, the difference for each addition of CH_2, becoming progressively less: the equivalent of refraction, on the other hand, increases uniformly for each addition of CH_2.

4. On comparing together compounds belonging to different series, the empirical formulæ of which differ only in the number of atoms of carbon, the density, and usually also the refractive index, is diminished by each additional atom of carbon: the specific refractive energy is, in some cases, increased, and in others, diminished, but the equivalent of refraction generally increases very uniformly.

5. When the proportion of hydrogen only is increased, the density, the index of refraction, the specific refractive energy, and the equivalent of refraction are all increased.

6. When the number of atoms of oxygen alone is increased, the density, the index of refraction, and the equivalent of refraction are all increased, whilst the specific refractive energy is diminished.

The equivalent of refraction, it appears, then, is always increased, whether hydrogen, oxygen, or carbon be added to the compound; but the amount of the increase is not uniform for each additional atom of the same element, being in some cases greater than in others, according as the chemical type of the compound varies.

In the case of mixtures, unattended by contraction, Dale and Gladstone find that the specific refractive energy is the arithmetical mean of that of its components; and they conclude, from the results of their entire investigation, that "every liquid has a specific refractive energy composed of the specific refractive energies of its component elements, modified by the manner of combination, and which is unaffected by change of temperature, and accompanies it when mixed with other liquids" (*Phil. Trans.* 1863, 337).

Dr. Gladstone (*Phil. Trans.* 1870, 9) has also found that the refraction equivalents of many gases and solids are not changed when these substances

are dissolved in water or alcohol, and that many elements retain their refraction equivalents even when in chemical combination, so that the refraction equivalent of a compound may often be calculated from those of its elements and the refraction equivalent of an element determined by the examination of one of its compounds with another element of which the refraction equivalent is known.

Some elements are found to have different refraction equivalents in different compounds, thus in ferrous salts that of iron is 12·0 and in ferric salts 20·1; again hydrogen in some compounds has an equivalent of 1·3 and in others of 3·5. The investigation of the refractive energy of compounds sometimes enables the chemist to obtain a glimpse of their internal structure, for instance, the hydrochlorate of camphene seems to be a compound of the formula $C_{10}H_{17}Cl$ and not a combination of hydrochloric acid with the hydrocarbon $C_{10}H_{16}$.

(106) *Fixed Lines in the Solar Spectrum; Fraunhofer's Lines; Bright Lines in Artificial Lights.*—Newton, by admitting a beam of solar light through a small circular aperture into a darkened room, and allowing it to fall upon a triangular prism of glass, obtained the magnificent coloured image known as the *solar spectrum,* which shades off by insensible gradations from the least refracted red into the most refracted or violet portion of the light. But it does not appear that any one, till Wollaston's time, a century later, examined the effect of admitting the light through a narrow slit, with sides parallel to those of the prism, and viewing it directly, by placing the eye immediately behind the prism (*Phil. Trans.* 1802, 378). Wollaston found that the spectrum so obtained was not, as it appeared to be by the ordinary mode of examination, a continuous stripe of light, but that it was crossed at right angles to its length by dark bands, which he supposed divided the colours of the spectrum from one another.

It was not, however, till 1815, that these dark bands were carefully examined, when the celebrated German optician, Fraunhofer, published a minute description of them, accompanied by a careful map, in which he figured more than six hundred of these lines, which have ever since borne the name of *Fraunhofer's lines.* The more important of these lines he distinguished by the letters of the alphabet, and in the uppermost spectrum shown in figs. 81 and 83, a few of them are given as points of comparison with other spectra.

In order to observe these lines, the sun's light, after admission through a narrow vertical slit into a darkened room, was allowed to fall upon a prism placed with its axis parallel to the slit, and at a distance of about 24 feet (7 or 8 metres) from it. The prism was fixed before the object-glass of a telescope of low power, in such a manner that the angle formed by the incident light with the first face of the prism, was equal to that formed by the refracted beam with the second face, so that the position of the prism was that in which the light is subjected to the minimum amount of deviation. This is consequently generally spoken of

as *the position of minimum deviation.* Under these circumstances Fraunhofer observed numberless vertical lines, varying in breadth and in strength in different parts of the spectrum. These bands were always visible, whatever was the solid or liquid medium used in the construction of the prism, and whether its refracting angle were great or small; and under all circumstances they preserved the same relative position in the respective coloured spaces in which they occur. This fixed position has enabled the optical observer to use these lines as points of reference by which the refractive indices of a great variety of bodies have been determined with precision.

When, however, the source of the light was varied, as if the flame of a candle, the light of the fixed stars,* or the spark from the electrical machine was made use of, a different set of lines was in each case observed to occur.

Beyond this fact—viz., the dependence of the position of the lines upon the source of the light employed—Fraunhofer was unable to ascertain anything connected with their cause.

The inquiry thus launched by Fraunhofer has been followed in four principal branches of research, which may be described as relating to—

a. Cosmical lines, or the black lines produced in the light of the sun, the planetary bodies, and the fixed stars.

b. Black lines produced by absorption, a class of phenomena discovered by Sir D. Brewster, in his observations upon the red vapours of nitrous acid.

c. Bright lines produced by the electric spark when taken between different metallic conductors.

d. Bright lines produced by coloured flames or by the introduction of different substances into flame.

I shall enter into some detail upon this subject, which has acquired great interest and importance from the remarkable investigations of Kirchhoff and Bunsen.

a. The cosmical lines admit of partial reproduction by means of photographs of the spectra in which they occur. Most of these lines shown by the photograph are, however, invisible to the eye, as they occur in that part of the spectrum which is more refrangible than even the violet rays. Edmond Becquerel (*Taylor's Scientific Memoirs,* 1843, iii. 537) was the first who received the

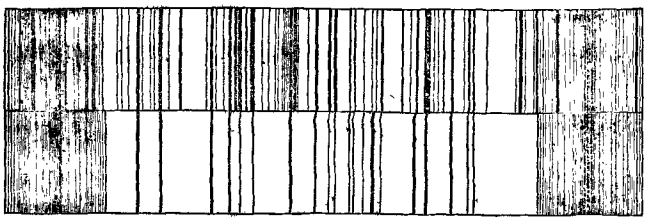
* The moon and the planets, including Venus, Jupiter, Saturn, and Mars, exhibit lines corresponding with those of the Sun. In the case of Jupiter, Saturn, and Mars, additional lines are also visible, owing to an absorptive action, due, as is believed, to the atmospheres surrounding these planets (Huggins and Miller, *Phil. Trans.* 1864, 421). Sirius shows different lines, and Castor others somewhat similar. Amongst the lines of Procyon, Fraunhofer recognised the solar line D, and in those of Capella and Betelgeux, both D and *b* (Brewster's *Edin. Journ. Science,* 1828, viii. 7). (109 *note.*)

impression of the spectrum with suitable precautions upon a Daguerreotype plate; and he made the important and interesting discovery that the inactive spaces in the portion of the chemical spectrum produced by visible rays, correspond accurately with the dark lines of Fraunhofer,—a discovery immediately afterwards corroborated by the independent observations of Draper, of New York, and subsequently confirmed in a remarkable manner for the invisible rays, by Stokes, who (*Phil. Trans.* 1852, 463) succeeded in rendering the lines in the most refrangible and extra-violet portions apparent to the eye, by his discovery that the fluorescent power of the spectrum is interrupted by inactive spaces, the position of which correspond accurately with the lines observed by Becquerel.

Mr. Rutherford, of New York, has since taken some very successful photographs of the solar spectrum. The photograph of the blue end only is six or seven feet long, and was taken in sections on account of the immense difference in the chemical activity of the light at the different parts, the exposure of the green portion being seven minutes, while in the ultra-violet only five seconds were required to produce a good impression.

Mr. Lockyer has also carefully photographed the more refrangible portions of the spectrum, in order to compare it with the spectra of the metals. In this way large numbers of lines have been discovered which are almost invisible, in consequence of the small amount of light in those parts of the spectrum. Fig. 80 *a*,

FIG. 80 *a*.

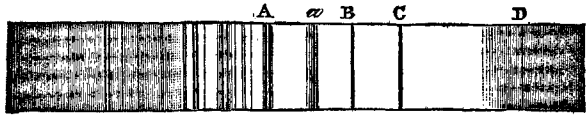


is copied from one of these photographs, showing the portion of the solar spectrum in the violet containing the two H lines, and below, for comparison, is shown the same portion as recorded by Angström from eye observations, the diagram being taken from a plate in the *Phil. Mag.* 1862 [4], xxiv. In some of the photographs, more than 100 lines have been counted between the broad bands, while Angström's map shows only 20.

Captain Abney has discovered a process by which the ultra-red rays may be photographed, and many more invisible lines be

found. (*Nature*, xiii. 432.) Fig. 80 *b*, is taken from one of Captain Abney's photographs, and published in his treatise on Photography (*Text-books of Science*, Longman's).

FIG. 80 *b*.



b. The absorption bands produced by coloured gases were first indicated in 1832 by Brewster (*Phil. Mag.* 1836, viii. 384), who found that the brownish-red vapours of peroxide of nitrogen have the remarkable power of absorbing the sun's rays in such a manner as to produce a series of dark bands in the spectrum of the light transmitted through it. Professors W. H. Miller and Daniell subsequently showed that the same effect is produced, whatever be the source of light employed. In the course of this investigation an important observation was made by Brewster, who noticed distinct lines and bands in the red and green spaces, which at other times wholly disappeared. This he found to be due to an absorptive action of the earth's atmosphere; for these bands were only visible when the sun approached the horizon. A few years later I had an opportunity myself, whilst examining the spectrum of diffused daylight in the afternoon during a violent thundershower, to observe the sudden appearance of a group of lines in the brightest part of the spectrum, between D and E, increasing in distinctness with the violence of the shower, and fading and disappearing as the rain passed away. These observations, therefore, prove that certain of the fixed lines in the solar spectrum are dependent upon the absorptive action exerted by the earth's atmosphere.* But the larger portion, it is supposed, are due to another

* Janssen (*Comptes Rendus*, 1863, lvi. 538) and J. P. Cooke have since studied the conditions under which these atmospheric bands are produced. Cooke (*Phil. Mag.* 1866 [4], xxxi. 337) has found that certain of them are connected with the moisture of the atmosphere, and these lines become more marked in proportion to the increase in the quantity of aqueous vapour. In October, 1864, Janssen observed a fire of pine wood across the Lake of Geneva at a distance of 21 kilometres, or after the light had traversed a stratum of rather more than 13 miles of moist air; and he found, on examining the spectrum at this distance, that certain atmospheric lines appeared, although the same flame, when viewed close at hand, presented no indication of such lines. A still more decisive observation was made by Janssen in the following manner (*Comptes Rendus*, 1866, lxiii. 289): An iron tube, 37 metres long, was enclosed in a wooden trough of the same length, and packed with dry sawdust; the ends of the iron tube were

cause, first suggested by Kirchhoff. Prof. Miller, of Cambridge, in conjunction with Daniell, followed up these experiments, and showed that other coloured vapours—viz., those of bromine, iodine, and euchlorine—possess this property (*Phil. Mag.* 1833, ii. 381).

Twelve years afterwards I myself made a numerous series of experiments upon the same subject (*Phil. Mag.* 1845 [3], xxvii. 81). The result of these experiments showed that mere existence of colour in a vapour does not indicate of necessity the existence of bands in its spectrum. The red vapours of tungstic chloride give no lines, while bromine vapour, which has to the eye the same colour, produces a remarkable series.

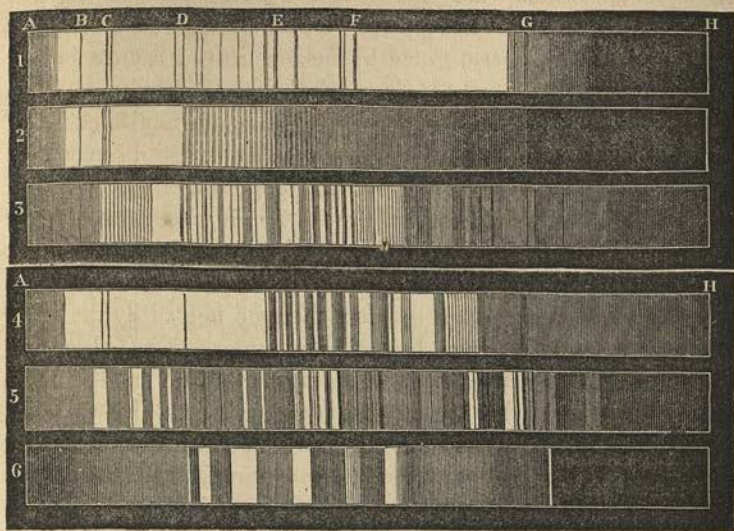
The probable position of the lines cannot be inferred from the colour of the gas: with the green oxychloride of manganese the lines are most abundant in the green, whilst with the red vapours of nitrous acid they increase in number and density as they advance towards the blue end of the spectrum. Simple bodies, as well as compounds, may produce lines; and two simple bodies, which singly do not produce them, may in their compounds occasion them abundantly; *e.g.*, neither oxygen, nitrogen, nor chlorine,* when uncombined, occasions lines, but some of the oxides, both of nitrogen and of chlorine, exhibit the phenomena in the most striking manner. There are, however, oxides both of nitrogen and chlorine, some of them coloured, which do not occasion the appearance of lines. We find also that lines may exist in the vapour of simple substances, as in iodine, which disappear in their compounds. This is exemplified in the case of hydriodic acid. Sometimes the same lines are produced by different degrees of oxidation of the same substances, a remarkable instance of which is furnished in the oxides of chlorine. In fig. 81, No. 1 shows the principal dark lines of the pure solar spectrum; 2 represents the effect of bromine; 3, that of peroxide of nitrogen, the system of lines which it furnishes being totally different from that of bromine, notwithstanding the close resemblance in colour of the two vapours; 4 shows the lines in the green vapours of oxychloride of manganese.

closed with thick plate glass, and the atmospheric air was displaced by steam, under a pressure equal to 7 atmospheres. The light of a powerful coal-gas flame, which has no lines of its own, was then made to traverse the tube, and the spectrum of the transmitted light was examined. In the less refrangible portion between the lines A and D of Fraunhofer, five obscure bands were seen, two of which are well marked; the appearance resembling that of this portion of the solar spectrum when viewed at sunset, especially after rain; and at the same time a general absorption of light was perceived in the blue and violet portions. The light transmitted had an orange or red tinge, which was deeper in proportion to the quantity of aqueous vapour. It appears from those observations, though at present no detailed measurements have been published, that the groups A, B, and C of Fraunhofer, and two groups between C and D, are due to the action of aqueous vapour in the atmosphere. Lieut. J. H. Hennessey (*Proc. Roy. Soc.* 1870, xix. 1, and *Phil. Trans.* 1875, 157) has observed in the Himalaya mountains, the atmospheric lines exhibited by the spectrum of the sun when near the time of setting.

* Though chlorine does not exhibit absorption lines when the light is passed through a thin layer of the gas, yet numerous lines have been observed on employing a tube 1 metre long.

c. On the Spectra of the Electric Spark.—Wollaston (*Phil. Trans.* 1802, 380) observed that the spectrum of the electric

FIG. 81.



spark is not continuous, and that it differs from that of ordinary sunlight, as well as from that furnished by the light of a candle. Fraunhofer also made a similar observation; but the first person who called attention to the important fact that the nature of the metals employed modifies the resulting spectrum, was Wheatstone, who, at the Dublin meeting of the British Association for 1835, read a paper "On the Prismatic Decomposition of the Electric, Voltaic, and Electro-Magnetic Sparks." In the abstract published in the Report of the Proceedings of the Association for that year, the author states that the spectrum of the electro-magnetic spark taken from mercury, as well as from zinc, cadmium, tin, bismuth, and lead in the melted state, consists of definite rays separated by dark intervals from each other; but the number, position, and colours of the bright lines vary in each case. The appearances are so different, that the metals may be readily distinguished from each other by this mode of examination. When the voltaic spark from mercury was taken successively in the ordinary vacuum of the air-pump, in the Torricellian vacuum, and in gaseous carbonic anhydride, the same results were obtained as when the experiment was performed in air, or in oxygen gas. The light, therefore, does not arise from the combustion of the metal.

Masson, in 1851 and 1855, in the course of his investigations on electric photometry (*Ann. Chim. Phys.* 1851 [3], xxxi. 295, and 1855 [3], xlv. 387), examined the spectra produced by various metals which were employed as dischargers to the Leyden jar, and also when heated by the voltaic arc, and gave drawings of the different spectra, made by means of the camera lucida. The spectra which he has given of the same metals as those examined by Wheatstone, are much more complicated than those described by the English philosopher. These discrepancies were subsequently explained by Angström (*Phil. Mag.* 1855 [4], ix. 327), who showed that owing to the intense heat of the electric discharges employed by Masson, he obtained two spectra simultaneously, one due to the metal, the other to the atmosphere itself, the constituent gases of which became heated by the spark to incandescence. Certain bright lines remarked by Masson as common to the spectra of all the metals were really these atmospheric lines. By causing the spark to pass between the same metals when immersed in various gases, the particular bright lines due to the metal remained unaltered, whilst the others, due to the gaseous medium, disappeared, and their place was supplied by new bright lines. Angström, in the course of his paper, suggests, though he does not distinctly state, the explanation of Fraunhofer's dark lines, subsequently brought forward by Kirchhoff. It appears,* however, that in 1853 Angström in his "Optic Researches" distinctly announced the same explanation of Fraunhofer's lines that was afterwards given by Kirchhoff; but from ignorance of the Scandinavian languages it was not known in this country till 1856.

In 1858 and 1859, an important series of investigations was published by Plücker (*Poggendorff's Annal.* 1858, ciii. 88, 151, civ. 113, 622, cv. 67, and 1859, cvii. 77, 497), relating to the character of the electric light produced by transmitting the secondary charge from Ruhmkorff's coil through narrow tubes filled with different gases, and subsequently exhausted as completely as possible. Vacuous tubes were thus obtained with only imponderable traces of various gases and vapours, including oxygen, hydrogen, nitrogen, chlorine, bromine, and iodine. Plücker found that each exhausted tube gave its own characteristic spectrum, and he measured with great care the principal bright lines visible in each. These results are very important in

* See Address of the President of the Royal Society, 1870. *Proc. Roy. Soc.* xix. 120.

relation to Kirchhoff's theory of the cause of the dark lines, which requires that the position of the bright lines thus obtained, should coincide with the black lines produced by absorption when light is transmitted through these different gases. Plücker's experiments show distinctly that this is not the case in these gases. Dr. Robinson subsequently investigated the effect of varying the pressure upon the nature of the electric spectrum of an incandescent gas (*Phil. Trans.* 1862, 939): he finds that the light is the most intense under ordinary pressures, though at low pressures bright lines appear which are not visible at the ordinary pressure of the gases.

Van der Willigen (*Poggendorff's Annal.* 1859, cvi. 617) made the interesting remark that, by placing in succession upon a pair of wires consisting of a metal which, like platinum, possesses few special bright lines of its own, small quantities of a weak solution of chloride of calcium, barium, or strontium, or of nitrate of calcium, &c., new bright lines are produced, and these lines are characteristic of the particular metal contained in each of these several compounds.

d. Spectra of Coloured Flames.—The first person who seems to have analysed coloured flames by means of the prism, was Sir J. Herschel, who describes briefly (*Edin. Phil. Trans.* 1822, ix. 455), the spectra of strontic, calcic, and cupric chloride, of cupric nitrate, and of boracic acid. The same observer, in the article LIGHT, *Encycl. Metrop.* 1827, 438, says:—"Salts of soda give a copious and purely homogeneous yellow, of potash a beautiful pale violet:" and he then gives a general statement of the results with the salts of calcium, strontium, lithium, barium, copper, and iron. He further continues,—"Of all salts the muriates [chlorides] succeed best, from their volatility. The same colours are exhibited also when any of the salts in question are put in powder into the wick of a spirit-lamp. The colours thus communicated by the different bases to flame, afford in many cases a ready and neat way of detecting extremely minute quantities of them."

The analysis of the spectra of artificial lights was resumed by Fox Talbot (Brewster's *Journal of Science*, 1826, v. 77). He there describes a method of obtaining a yellow monochromatic light by the use of an ordinary spirit-lamp with a cotton wick fed with dilute alcohol holding common salt in solution. He found the same effect, whether chloride, sulphate, or carbonate of sodium was employed.

Nitrate, sulphate, chlorate, and carbonate of potassium agreed

in giving a bluish-white tinge to the flame. By burning a mixture of nitre and sulphur, he observed a red line of low but definite refrangibility, which he regarded as characteristic of the salts of potassium, as the yellow line is of the salts of sodium. He concludes his paper with the following observation, which follows some remarks upon certain experiments of Herschel's:—"If this opinion should be correct and applicable to the other definite rays, a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise require a laborious chemical analysis to effect."

In the *Phil. Mag.* for 1834 [3], iv. 115, Fox Talbot further showed how, notwithstanding the similarity in colour of the light of lithium and strontium, they can at once be distinguished by means of the prism. He says,—"The strontia flame exhibits a great number of red rays, well separated from each other by dark intervals, not to mention an orange and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty, if not more, than any other known method."

The spectra of coloured flames were further examined in 1845 by myself, and an account of these experiments was given in a paper read that year before the Chemical Section of the British Association, at Cambridge. (*Phil. Mag.* 1845 [3], xxvii. 81.)

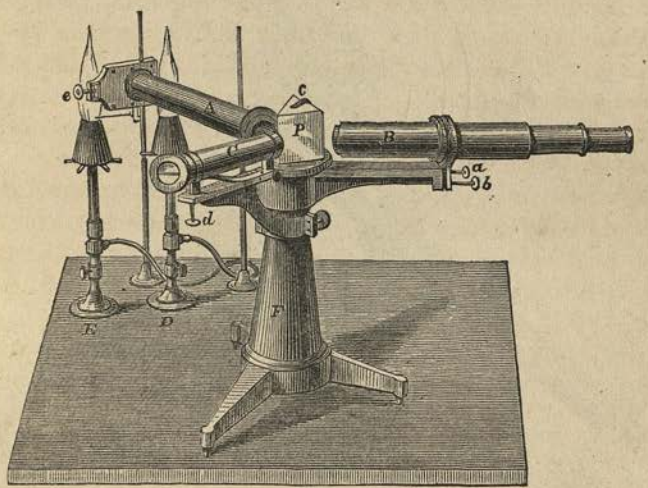
In these experiments an alcohol lamp, fed with the solution of the compound the flame of which was to be examined, and a common wick supported in a small glass tube, furnished the flame. The lamp was placed opposite the vertical slit, through which diffused daylight could also be transmitted at pleasure. Fraunhofer's lines thus served as points of comparison of the different flames. The paper was illustrated by coloured lithographs of various spectra, including those of cupric chloride, boracic acid, strontic nitrate, calcic and baric chlorides, in minute detail. The green light produced by burning a solution of cupric chloride in alcohol, for instance, gives the spectrum shown in fig. 81, No. 5, and that furnished by an alcoholic solution of boracic acid is represented in No. 6. Numerous other spectra were also described, including those of the chlorides of sodium, manganese, and mercury, and of a large number of other metals.

(107) *Spectrum Analysis.*—But it is to Kirchhoff and Bunsen (*Poggendorff's Annal.* 1860, cx. 161) that we are indebted for reducing the prismatic observation of flame tinged by the salts of different metals to a simple and systematic method of qualitative analysis for the alkalies and alkaline earths; and they have contrived a *spectroscope* by which the different spectra may be conveniently examined and compared with one another.

Fig. 82 exhibits a very complete form of the instrument adapted to a single prism (*Poggendorff's Annal.* 1861, cxiii. 374). It is an improvement on the

instrument used by Swan and by Masson; including a scale for ascertaining the position of the lines in different cases, as well as a reflecting prism, by which two spectra can be compared side by side. P represents a flint-glass prism, supported on the cast-iron tripod F, and retained in its place by the spring, *c*. At the end of the tube, A, nearest the prism, is a lens, placed at the distance of its focus for parallel rays from a vertical slit at the other end of the tube. The width of the slit can be regulated by means of the screw, *e*. One-half of this slit is covered by a small right-angled prism designed to reflect the rays proceeding from the source of light, D, down the axis of the tube, whilst the rays from the source of light, E, pass directly down the tube. By this arrangement the observer stationed at the end of the telescope B, is able to compare the spectra of both lights, which are seen one above the other, and he can at once decide whether their lines coincide or differ. *a* and *b* are screws for adjusting the axis of the telescope so as to bring any part of the slit at *e* into the centre of the field of vision. The telescope, as well as the tube, C, is movable in a horizontal plane, around the axis of the tripod. The tube C contains a lens at the end next to the prism,

FIG. 82.

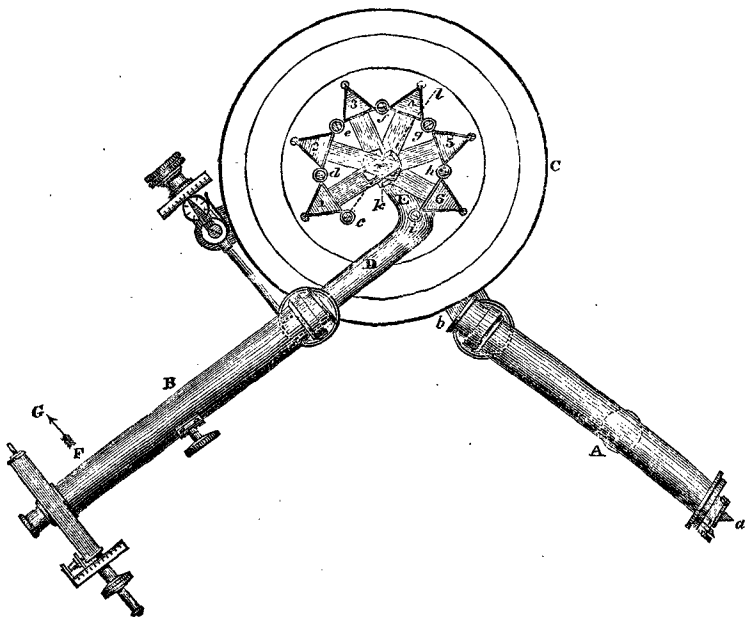


and at the other end is a scale formed by transparent lines on an opaque ground; it is provided with a levelling screw, *d*. When the telescope has been properly adjusted to the examination of the spectrum, the tube C is moved until it is placed at such an angle with the telescope and the face of the prism, that when light is transmitted through the scale, the image of this scale is reflected into the telescope from the face of the prism nearest the observer. This image is rendered perfectly distinct by pushing in the tube which holds the scale nearer to the lens in C, or withdrawing it to a greater distance, as may be required. The reflected lines of the scale can then be employed for reading off the position of the bright or dark lines of the spectrum, as both will appear simultaneously, overlapping each other, in the field of the telescope. By turning the tube C round upon the axis of the tripod, any particular line of the scale can be brought to coincidence with any desired line of the spectrum. Stray light is excluded by covering the stand, the prism, and the ends of the tubes adjoining it, with a loose black cloth. The dispersive power upon the spectrum may be much increased by using several prisms instead

of one: in the experiments of Kirchhoff upon the solar spectrum, he used four prisms; Huggins (*Phil. Trans.* 1864, 139) in his observations on the spectra of the metals obtained with the electric spark employed six prisms, and Gassiot has used an apparatus with nine prisms. Much care is required in placing the prisms: the refracting edge of each prism must be truly vertical, and the position of minimum deviation for the rays to be observed must be obtained.

Mr. Browning has constructed an ingenious form of automatic spectroscope in which the light passes through a train of six prisms. The prisms are mounted on triangular supports which are linked to one another and to the observing telescope in such a manner that on moving the latter all the prisms are maintained at the angle of minimum deviation for the particular ray under observation. The action of this spectroscope will be seen by an inspection of fig. 82 *a*, which is a plan of the latest form of the instrument. A is the collimator with

FIG. 82 *a*.



the slit and small reflecting prism at *a*, the rays transmitted by the slit are rendered parallel by the lens at *b*, the beam then traverses the prisms 1, 2, 3, 4, 5, and 6, and the spectrum is observed through the telescope B. The prism 1 is attached to the plate C by a screw passing through the triangular support at the angle *c*, nearest to the collimator, so that it may turn on this axis through a small arc. The prism is also attached to prism 2 by a screw *d* placed at the other end of its base, and the other prisms are similarly linked together at *e*, *f*, *g*, and *h*, the last prism 6 being linked by the screw *i* to the arm D which bears the observing telescope. The support of each prism carries, rigidly fixed to it, a flat brass bar placed at right angles to the base of the prism and which has a slot at its extremity. The arm D is bent at right angles, and its shorter portion E is also slotted. In the plate C a slot is cut in the direction *l c*, that is, towards the fixed angle of prism 1; and under the plate there is a dovetail piece sliding parallel to the slot and carrying a pin *k*, which is passed through

the slot in the plate and through the seven slotted pieces attached to the prisms and telescope.

If it is required to observe the more refrangible end of the spectrum, the telescope B must be moved in the direction F G. This moves the train of prisms, causing all the prisms to approach the central pin *k*, diminishing the diameter of the circle of which *k* is the centre, and to which the bases of the prisms are tangents. The first prism being fixed at one angle can only move to a small extent, the second will move a little more, and so on, and by arranging the circle of the prisms to a size which will accord with the refractive index of the glass, the instrument is so fitted that the refracted ray is always parallel to the base of the prism through which it is passing, or in other words, each prism is at the angle of minimum deviation.

Still more powerful spectroscopes have been constructed, in which the light is passed first through the lower half of the prisms, and is then reflected through the upper half by means of a right-angled prism with its hypothenuse vertical placed opposite to the last prism. Mr. Browning has made an instrument in which the light passes no less than four times through the prisms. In these spectroscopes both the collimator and the observing telescope are fixed, and the different portions of the spectrum are brought into view by altering the position of the train of prisms. The prisms can be readily detached from the stand, and to each of them the reflecting prism can be fixed, so that any number less than the whole train can be employed.

The extraordinary delicacy of certain of these spectrum reactions was indicated by Swan (*Edin. Phil. Trans.* 1857, xxi. 413), who measured it for sodium, by the only accurate method, namely, by dissolving a weighed quantity of the salt in a known quantity of water, and he thus determined with precision the limit of the reaction. Bunsen and Kirchhoff attempted to estimate the sensitiveness of the reaction by deflagrating a given weight of the various salts in the room in which they were experimenting, and diffusing the vapour mechanically through the air, increasing the quantity of the salt, until a gas flame showed the reaction of the peculiar metal, due to particles in suspension. But it is obvious that this ingenious method does not admit of precision, and is liable to lead to an exaggerated estimate of the delicacy of the reaction, from the impossibility of ensuring uniformity in the diffusion of the salt.

The sodium reaction is the most sensitive of all: by its means Swan could detect $\frac{1}{2500000}$ of a grain of sodium; and so extensively is common salt diffused, that scarcely any flame can be obtained in which the indication of sodium is absent.

Having observed the position of the bright lines produced by introducing into the flame of a Bunsen gas-burner the chlorides of the metals of the various alkalies and alkaline earths, each of which had been purified for these experiments with great care, Bunsen and Kirchhoff constructed a chart in which the different lines were laid down for each, and they were able, by observing

the position of the lines obtained when a mixture of various chlorides was introduced into the flame, to ascertain the presence of these different metals with sufficient readiness to use the method for the purposes of qualitative analysis. The rapidity with which the result is obtained by a practised observer, and the minuteness of the quantity required for the examination, gives this method a superiority over any other now in use for the qualitative analysis of the alkalies and alkaline earths; moreover, the circumstance that the mere inspection of a source of light furnishes information respecting the composition of the bodies undergoing combustion or volatilization within it, extends the mode of inquiry over distances limited only by the distance through which the object is visible; we are thus furnished with a method of analysis which is applicable to the luminous atmosphere of the sun, the stars, as well as to the light of the planetary bodies, and even of the nebulæ. This circumstance invests the subject with an interest like that which attends the employment of the telescope; at the same time the minuteness of its search enables it to reveal, like the microscope, quantities of matter indefinitely small.

This minuteness in its scrutiny has already, in the hands of Bunsen and Kirchhoff, led to the discovery that many bodies, such as lithia and strontia, formerly supposed to be rare, are really widely distributed in minute quantities. It also led them to discover the two new alkalies *cæsia* and *rubidia*, the first named from *cæsius*, "sky-coloured," in allusion to two characteristic blue lines in its spectrum; the second from *rubidus*, "dark red," owing to the existence in its spectrum of two red lines of remarkably low refrangibility.

These bases were found in the course of an examination by the prism of the residue of the mother-liquor from the Durkheim spring, when the occurrence of these hitherto unobserved lines induced Bunsen to make a minute chemical examination of the water which furnished them. The inquiry showed that in every ton of the original water, about three grains of cæsic chloride, and rather less than four grains of rubidic chloride, were present. These two salts so closely resemble potassic chloride in properties, that it would have been impossible to have ascertained their existence in the minute proportion in which they occur, but for the method of spectrum analysis. To these bodies Crookes, in May, 1861, added a third metallic element, *thallium*, so called from θαλλὸς, a budding twig, in allusion to the brilliant green line in which the luminosity of its spectrum is concentrated. This body was found in minute quantity in the residue from a sul-

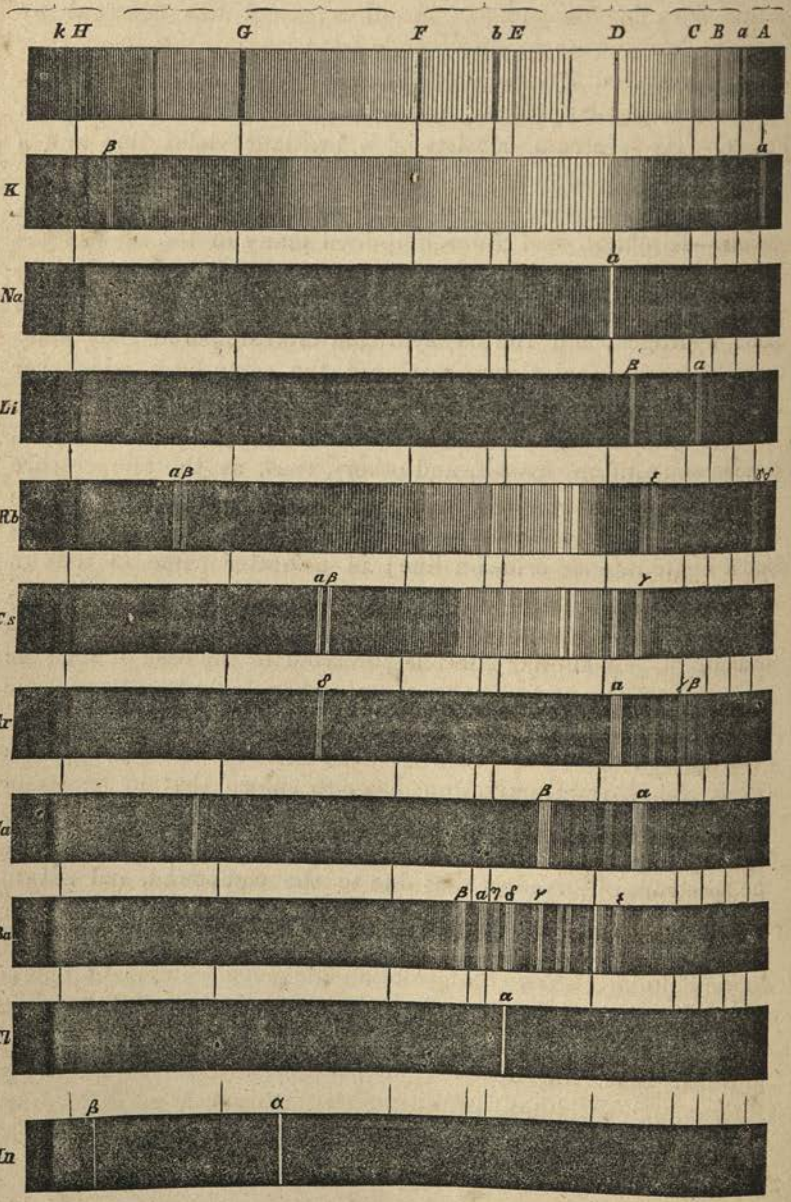
phuric acid chamber at Tilkerode, in the Hartz: and it has since been found in minerals from various other localities, particularly in Belgian pyrites. In the year 1863 a fourth metal was found by the spectrum examination of one of the Freiberg zinc ores, by Reich and Richter (*Journ. pr. Chem.* 1863, lxxxix. 441, and xc. 172); its discoverers named it *indium*, from its pair of characteristic lines in the indigo. Another metal was detected by Lecoq de Boisbaudran in zinc blende from the mine of Pierrefitte, valley of Argeles, Pyrenees (*Comptes Rendus*, 1875, lxxxi. 493). It has been named *gallium*, in consequence of its discovery in France. Its spectrum consists of a brilliant violet line and a feeble band.

(107 *a*) *Influence of Different Temperatures—Spectra of Compounds.*—Kirchhoff and Bunsen ignited many of the salts of the different metals in flames of very varying temperature, including those of sulphur, carbonic disulphide, diluted alcohol, carbonic oxide, hydrogen, and the oxyhydrogen mixture; and they state that the same metal always produced the same lines, whichever flame they employed to heat it.

It has, however, since been observed by Tyndall, Frankland, Roscoe and Clifton, myself, and others, that, as the temperature rises, a new series of bands become visible in certain cases. The spectrum of lithic chloride, in the flame of a Bunsen burner, gives but a single intense crimson line; in a hotter flame, as that of hydrogen, it gives an additional orange ray; and in the oxyhydrogen jet, or the voltaic arc, a broad brilliant blue band comes out in addition. A similar effect is perceived in the case of metallic iron, of thallium, and of other metals when heated by the voltaic arc, which at elevated temperatures furnish much more complicated spectra than when less intensely heated. A. Mitscherlich (*Pogg. Annal.* 1862, cxvi. 499) has also shown that in flames of low temperature, the lines produced by different compounds of the same metal vary with the compound employed: in these cases the spectrum observed is that due to the compound, and not to its elementary constituents; the spectrum of metallic copper, for example, differs considerably from that of an alcoholic solution of cupric chloride, whilst that from an alcoholic solution of cupric iodide differs from both. These observations do not destroy the value of spectrum examination as a means of qualitative analysis, provided that the operator adopts the method laid down by Bunsen and Kirchhoff, who introduce into a coal-gas flame, furnished by one of Bunsen's gas-burners, a chloride of the metal for examination, supported on a loop of platinum wire.

The spectra figured by Bunsen and Kirchhoff were obtained in each case by acting upon the chlorides of the several metals; and those of the alkaline earths represent, according to the re-

FIG. 83.



searches of Diacon (*Ann. Chim. Phys.* 1865 [4], vi. 25), mixed spectra, due in part to the oxides, and in part to the chlorides of the metals. In the memoir just cited Diacon has confirmed the observation of A. Mitscherlich that many classes of binary compounds possess proper spectra, differing from those of the pure metals both in the arrangement and the number of the lines.

During the decomposition of the iodides, bromides, chlorides, and fluorides of certain metals in the flame of the blow-pipe fed usually with air, or in particular cases with oxygen, brilliant lines were observed, due to the halogen present in the compound; but these lines, the duration of which is very variable, are always accompanied by the spectrum due to the oxide of the metal.

By heating even the easily decomposable chlorides of certain metals in a hydrogen flame fed with excess of chlorine, the special spectrum of the chloride may frequently be obtained, when it is seen to differ from the spectrum obtained from a flame supplied with oxygen. For example, in a chlorinating flame, the chlorides of the alkali-metals potassium and sodium give no spectrum at all; the spectrum of lithic chloride is not altered, and pure strontic chloride does not show the orange and blue lines usually regarded as characteristic of the compounds of strontium.

The spectrum reactions of the halogens, however, are not sufficiently delicate, nor can they be as yet secured with sufficient facility to render the spectrum test superior to the methods in use by the ordinary mode of analysis: though both Mitscherlich (*Pogg. Annal.* 1864, cxxi. 459) and Diacon give processes for applying the spectroscope for the discrimination of the halogens when in combination.

The first spectrum shown in fig. 83 exhibits some of the fixed dark lines of the solar spectrum contrasted with the position of some of the most important bright lines furnished by the spectra of the alkalies and alkaline earths, when their chlorides are heated upon a loop of platinum wire introduced into the flame of a Bunsen gas-burner. The characteristic bright lines in the case of each metal are distinguished by the letters of the Greek alphabet, the most strongly marked lines being those indicated by the earliest letter.

Amongst the various spectra, that of thallium and those of the alkali-metals are the simplest. In the potassium spectrum the most characteristic bright lines are the red line K α, and violet line, K β. A copious diffused light fills up the central portion of the spectrum. In the case of sodium, nearly the whole of the light is concentrated on the intense yellow double line, Na a. In

the lithium spectrum; a crimson band, Li α, is the prominent line; Li β is seldom visible; but at the elevated temperature of the voltaic arc, an additional blue line becomes very intense. In the spectrum of cæsium, a good deal of diffused light is visible, but the two lines in the blue, Cs α and Cs β, are strongly marked, and may be seen when a quantity of the chloride not exceeding $\frac{1}{170000}$ of a grain of the pure salt is used, or $\frac{1}{7000}$ of a grain if diluted with fifteen hundred times as much lithic chloride. Rubidium is not distinguishable in quantities quite so minute. The lines, Rb α and Rb β, in the blue, and Rb γ in the red, are almost equally characteristic, but about $\frac{1}{33000}$ of a grain of the chloride is required to render them visible. Thallium is recognised by the single intense green line Tl α. The spectra of the alkaline earths are equally definite though more complicated; generally speaking, the elements of higher atomicity give more complex spectra.

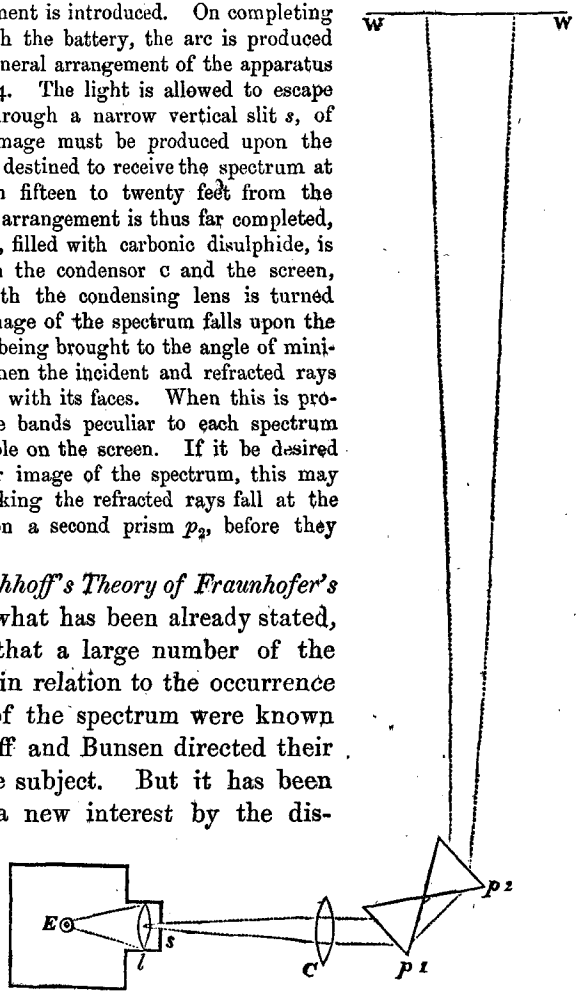
The salts which are most readily volatilized, such as the chlorides, bromides, and iodides of the different metals, give the most brilliant spectra. But it is only in the case of the alkalies and the alkaline earths that the spectra thus obtained are characteristic. Where the spectra of the other metals are required, recourse must be had to Wheatstone's method of taking electric sparks, between wires consisting of the metal of which the spectrum is required; and the electric sparks may conveniently be procured by the employment of Ruhmkorff's coil. The temperature obtained in this way is very intense, and developes bright lines not produced by the heat of ordinary flames. When a compound gas or vapour is made the medium of the electric discharge, the spectra produced are those of the elementary components of the gas. It seems as though, at these intense temperatures, chemical combination were impossible; and oxygen and hydrogen, chlorine and the metals, may therefore all coexist in a separate form, although mechanically intermingled.

The application of these processes of optical analysis to the examination of furnace flames, at different stages of various processes in the arts, cannot fail to afford information of high interest, which can be obtained in no other way. Roscoe has already applied it successfully in studying the Bessemer process for steel. Mr. Snelus, of the Dowlais Iron Works, has recently made some further researches on the flame from the Bessemer converter.

(108) *Projection of Spectra on a Screen.*—When it is desired to render the lines produced by the spectra from different metals visible to a large audience,

they may be shown by the employment of the voltaic battery. About forty pairs of Grove's construction will answer well. The wires of the battery must be connected with the carbon electrodes of a Duboscq's electric lamp. The metals to be burned are supported upon the lower or positive electrode made of the hard carbon deposited in the gas retorts: and when the salts of the metals are to be employed, two or three vertical holes are drilled into the upper end of the charcoal point, and into these the salt for experiment is introduced. On completing the connexion with the battery, the arc is produced as usual. The general arrangement of the apparatus is shown in fig. 84. The light is allowed to escape from the lamp through a narrow vertical slit s, of which a distant image must be produced upon the white screen w w, destined to receive the spectrum at a distance of from fifteen to twenty feet from the lamp. When the arrangement is thus far completed, a hollow prism p_1, filled with carbonic disulphide, is interposed between the condensor c and the screen, and the lamp with the condensing lens is turned round until an image of the spectrum falls upon the screen, the prism being brought to the angle of minimum deviation, when the incident and refracted rays form equal angles with its faces. When this is properly adjusted, the bands peculiar to each spectrum are distinctly visible on the screen. If it be desired to obtain a longer image of the spectrum, this may be effected by making the refracted rays fall at the proper angle upon a second prism p_2, before they reach the screen.

FIG. 84.



(109) *Kirchhoff's Theory of Fraunhofer's Lines.*—From what has been already stated, it is obvious that a large number of the principal facts in relation to the occurrence of the bands of the spectrum were known before Kirchhoff and Bunsen directed their attention to the subject. But it has been invested with a new interest by the discovery of the new metals, cæsium, rubidium, thallium, indium, and gallium, and particularly by a theory of Kirchhoff's which embraces and generalizes the greater number of the phenomena. This theory we shall now consider.

It is to be remembered that the spectrum produced by the ignition of a solid or of a liquid always yields a *continuous* band of light, containing rays of all degrees of refrangibility within the

range of its two extremes; but the same body, when converted into vapour, may produce a luminous atmosphere which may emit light of certain definite refrangibilities only, so as to produce a spectrum consisting of a series of bright bands of particular colours, separated from each other by intervals more or less completely dark. Bearing these facts in mind, the theory proposed to account for Fraunhofer's lines will be readily understood.

In 1858, Balfour Stewart published (*Edin. Phil. Trans.* 1858, xxii. 1) a paper on the law of exchanges in radiant heat, and in the following year the subject was taken up by Kirchhoff, who arrived at the same conclusions as Stewart, independently; and the German philosopher extended his theory to the phenomena of light as well as those of heat. The conclusions at which he arrived may be thus stated: That when any substance is heated or is rendered luminous, rays of a certain and definite degree of refrangibility are given out by it; whilst the same substance has also the power of absorbing rays of this identical refrangibility.

Sodium, for example, when vaporized at a high temperature emits an intensely brilliant yellow light, which is concentrated into two closely contiguous bands or bright lines coincident in position with Fraunhofer's double black line D in the solar spectrum. Fraunhofer had himself observed the exact coincidence of the double-black line D in the solar spectrum, with the double bright line in artificial lights, now known to be characteristic of sodium. If through a flame coloured by sodium, the more powerful light of the charcoal points or ignited lime be transmitted, the continuous spectrum due to this stronger source of light is interrupted by a double *black* line coincident with the solar black double line, D.* Kirchhoff has also ascertained that certain of the bright bands in the spectra of potassium, lithium, barium, and strontium, may in like manner be reversed, and I have found that some of the strongest lines in the blue in the spectrum of copper may be similarly reversed.

Now Kirchhoff has applied these facts to the explanation of

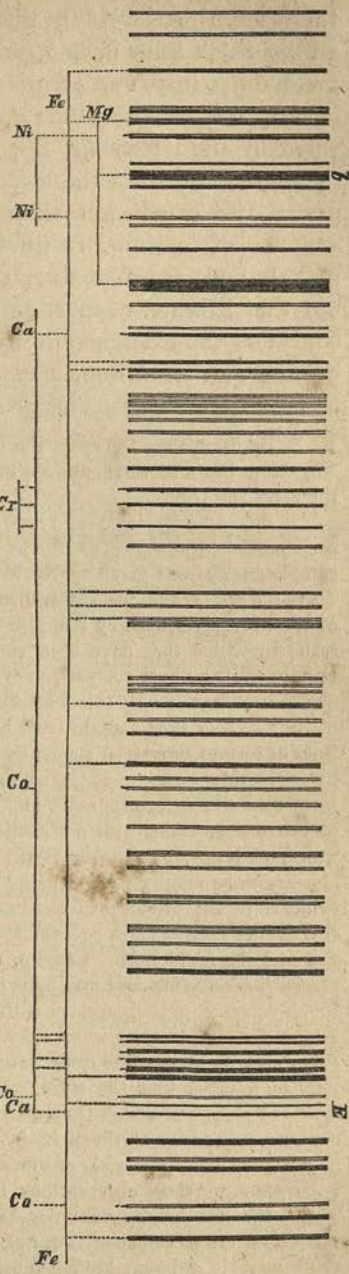
* Foucault (*Journal de l'Institut*, Feb. 7th, 1849) had already made this observation in a particular instance. He caused the image of the sun to fall exactly on the voltaic arc, and by viewing this compound light through a prism, he observed that the double brilliant line of the arc coincided exactly with the double black line of the solar light, and when they overlapped, the black line of the solar spectrum was rendered considerably more intense. This absorption by a heated gas of rays of the same refrangibility as those which it emits, is not without an analogy in the case of sound; for a stretched string will absorb the vibrations of a second string in unison with itself, and will in consequence itself respond to the note when sounded by the second string.

Fraunhofer's dark lines. He supposes that in the luminous atmosphere of the sun, the vapours of various metals are present, each of which would give its characteristic system of bright lines; but behind this incandescent atmosphere containing metallic vapour, is the still more intensely heated solid or liquid nucleus of the sun, which emits a brilliant continuous spectrum containing rays of all degrees of refrangibility. When the light of this intensely heated nucleus is transmitted through the incandescent photosphere of the sun, the bright lines which would be produced by the photosphere *are reversed*; and Fraunhofer's black lines are only the reversed bright lines which would be visible if the intensely heated nucleus were no longer there.

Kirchhoff has proceeded to test this theory by submitting the solar spectrum to a most minute investigation (*Researches on the Solar Spectrum, and on the Spectra of the Chemical Elements,* translated by Roscoe, and published in a separate form).

The opposite diagram is copied from a small portion of Kirchhoff's detailed drawing, including the part of the spectrum extending from E to *b* (fig. 85), and he states that for every bright line in the spectrum of iron there is a corresponding black line in the solar spectrum. About sixty such lines occur be-

Fig. 85.*



* For want of space, the figure is arranged vertically instead of across the page. The upper extremity is the most refrangible end.

tween D and F, and in the small portion contained in the figure there are thirteen such lines indicated by the mark *Fe*.* The strong black lines near *b*, marked *Mg*, coincide with the brilliant green lines in the spectrum of magnesium. Chromium, nickel, cobalt, and calcium, also give less distinctly marked lines, indicated by the letters *Cr*, *Ni*, *Co*, and *Ca*.

Kirchhoff, from these and other more extended observations, draws the conclusion that in the atmosphere of the sun the vapours of sodium, magnesium, calcium, iron, chromium, and nickel, and possibly zinc, cobalt, and manganese, are present; but that lithium, copper, and silver are not present. Angström considers the existence of hydrogen, aluminium, and probably of barium and strontium, may also be inferred.†

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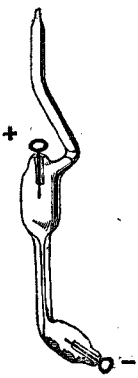
* By examining the spectrum of the electric arc passing from poles of iron Angström has discovered no less than 460 lines corresponding to black lines in the solar spectrum.

† Subsequently to these researches of Kirchhoff, Donati, Secchi, and Airy, each published observations on the spectra of some of the fixed stars, and a more complete series was given by Rutherford (*Silliman's Journal*, 1863, xxxv. 71). In the *Phil. Trans.* for 1864, already quoted, is a paper on the spectra of some of the heavenly bodies, by Huggins and W. A. Miller, describing a form of apparatus by which they have been enabled, by a method of simultaneous observation, to effect a direct comparison of the spectra of the heavenly bodies with those of different metals. By this means they have discovered that the spectra of many of the brighter stars contain dark lines corresponding in position with the bright lines of certain terrestrial elements. For example, in the red star Aldebaran they observed lines corresponding with those of sodium, magnesium, hydrogen, calcium, iron, bismuth, tellurium, antimony, and mercury. In the remarkable spectrum of the orange-tinted star α Orionis, the lines of sodium, magnesium, calcium, iron, and bismuth were observed. The spectrum of β Pegasi, though fainter, appears to be similar to that of α Orionis. The brilliant white star Sirius gives evidence of the presence of sodium, magnesium, hydrogen, and iron. α Lyræ and Pollux both contain sodium and magnesium; the former also shows hydrogen and the latter iron. Capella, Arcturus, α Cygni, and Procyon, all show the presence of sodium, and no doubt of various other terrestrial elements also, but the comparison of their spectra with the telluric elements is at present incomplete. About forty other stars were examined less perfectly by the same observers: in every case numerous fine lines were seen crossing the stellar spectrum. Hence it may be inferred that the stars, while differing the one from the other in the kinds of matter of which they consist, are all constructed upon the same plan as our sun, and many of them, if not all, are composed of matter identical, at least in part, with the materials of our system.

Extending these observations from the stars to the nebulæ, Huggins ascertained that the brighter nebulæ, including those known as planetary nebulæ, and certain others of sufficient luminosity to admit of such examination, give spectra of an entirely different kind. Their light is greenish blue, and is almost monochromatic, being nearly all concentrated into a single bright line, which coincides in position with the bright line in the spectrum of nitrogen about midway between the lines *b* and F of the solar spectrum. In some nebulæ a narrower and much

Plücker and Hittorf (*Phil. Trans.* 1865, 1) found that certain elements, such as sulphur and nitrogen, give two different spectra, the spectrum at a very elevated temperature being entirely different from that at a lower temperature, the two not having any line or band in common. Those formed at the lower temperature are designated spectra of the first order, those at the higher, spectra of the second order. With sulphur, for example, the following experiments may be made:—A tube of the form shown in fig. 86, consisting of two wide portions connected together by a capillary tube, is prepared with glass of difficult fusibility: into this sulphur is introduced, and the last traces of air having been removed, the whole is hermetically sealed. The tube having been placed in the proper position before the slit of the spectroscope, is gently warmed by a spirit-lamp, and sparks from an induction coil and Leyden jar are transmitted by the wires — +. As the temperature of the tube is raised, the pressure of the sulphur vapour increases, and the first spectrum increases in brilliancy, whilst at the same time the resistance to the passage of the spark continues to increase, and as a necessary consequence the temperature of the discharge continues to rise. The brilliancy of the spectrum gradually increases, and then suddenly the first spectrum vanishes, and is instantaneously displaced by the second spectrum, which is very rich in brilliant lines. On removing the spirit-lamp the temperature falls and the first spectrum reappears, whilst the second vanishes. Nitrogen even appears to give three different spectra; two of these are of the first order.*

Fig. 86.



fainter, more refrangible line was seen, and in a few a third still fainter, corresponding in position with the hydrogen line, F.

Such of the nebulæ as exhibit spectra of this kind can no longer be regarded as aggregations of suns of the same order as those to which our own sun and the fixed stars belong. "In place of an incandescent solid or liquid body transmitting lights of all refrangibilities through an atmosphere which intercepts by absorption a certain number of them, such as our sun appears to be, we must probably regard these objects, or at least their photo-surfaces, as enormous masses of luminous gas or vapour. For it is alone from matter in the gaseous state that light consisting of certain definite refrangibilities only, as is the case with the light of these nebulæ, is known to be emitted." (Huggins, *Phil. Trans.* 1864, 442.)

* Generally speaking, spectra of the *first order* may be obtained by transmitting the secondary discharge from an induction coil through an exhausted tube, which had previously been filled with the gas intended for experiment.

In the case of hydrogen the three characteristic bright bands of its ordinary spectrum become broader and broader as the intensity of the current is gradually increased, until the light becomes nearly continuous; the violet band expands first, whilst the red always preserves a certain definite character.

In the case of sodium, the bright lines at D gradually expand and coalesce, as the intensity of the current is increased; finally, this band expands, and becomes traversed by two black absorption lines coincident in position with the original bright lines.

Oxygen, chlorine, bromine, iodine, and phosphorus furnish only a single spectrum; these spectra are of the second order, and are figured in the memoir above cited. Arsenic and mercury also give spectra of the second order only. The general appearance of the first spectrum of a gas or vapour consists of broad luminous bands, generally nearly equidistant, and very similar one to the other throughout the particular spectrum. These bright bands are crossed by numberless dark lines, as well defined as those of Fraunhofer. The general character of the second spectrum is that of brilliant bands upon a more or less luminous ground. These bright bands have a breadth regulated by the width of the slit of the spectroscope.

Frankland and Lockyer (*Proc. Roy. Soc.* 1869, xvii. 288) investigated the spectra obtained by passing electric sparks from an induction coil through various gases at different pressures, and they find that under a pressure of 10 atmospheres hydrogen gives a perfectly continuous spectrum; on diminishing the pressure the spectrum gradually breaks up into lines, the red line corresponding to the Fraunhofer line c being the first to become definitely separated. At the atmospheric pressure the red line is sharply defined, but the green band corresponding to Fraunhofer's F line is wide and nebulous. On reducing the pressure (which was done by connecting the tube through which the sparks were passed with a Sprengel's pump and a pressure gauge) the green line became narrower and narrower until at a very low pressure the line was as thin as the red line. The breadth of the red line is also diminished during this process, but not nearly to the same extent as the green one.

(109 *a*) During the last few years many investigations have been prosecuted, and with great success, to determine the constitution of the sun. Astronomers have known for many years that, during the eclipses of the sun, red flames were observed protruding beyond the edges of the dark moon, and which are only visible during total eclipses, in consequence of the brilliancy of the white light of the sun and the very intense illumination of the earth's atmosphere. Various explanations have been given of these phenomena: by some they were supposed to belong to the sun, and by others to the moon. In the eclipse of 1860 it was

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Such spectra of the first order are usually succeeded by those of the *second order*, when the secondary discharge is made through the tube, whilst at the same time a Leyden jar is used, one of the insulated secondary wires being connected with the outer coating and the other with the inner coating of the jar.

shown by Mr. Warren de la Rue's photographs that these red protuberances belonged exclusively to the sun, as they were observed to remain stationary whilst the moon passed over the sun. The first systematic examination of these flames by the spectroscope was made during the eclipse of Aug. 18, 1868. Observations were conducted in India by Capt. Haig, Capt. Tanner, Mr. Kero Laxuman (*Proc. Roy. Soc.* 1868, xvii. 74), and Capt. Herschel (*Proc. Roy. Soc.* 1868, xvii. 104). Captain Haig saw in the spectrum of two of the red flames "two broad bright bands quite sharply defined, one rose-madder and the other light golden," which "were soon lost in the spectrum of the moon's edge just before emergence, which had also two well-defined bright bands (one green and one indigo) about a quarter of the width of the bands in the spectra of the flames."

The spectrum of the prominence seen by Capt. Herschel consisted of "three vivid lines, red, orange, blue: no others, and no trace of a continuous spectrum." The orange line Capt. Herschel considered coincident with the line D, he believed that the blue line corresponded with F, and was even more doubtful with regard to the red line, which he thought might be C, or less likely B.

As early as 1866, Mr. J. Norman Lockyer devised a method by which the red flames might be examined at any time, and without waiting for a total eclipse, an event of rare occurrence and of such short duration as to render observations on the protuberances difficult or impossible except under favourable atmospheric conditions. Assuming that the red flames were caused by the light emitted by incandescent gases or vapours, and the spectrum of which might be presumed to consist of bright lines only, Mr. Lockyer thought that, by using a spectroscope of very great dispersive power, it might be possible to elongate the spectrum of the white light of the sun and of the brilliantly illuminated terrestrial atmosphere to such an extent that the intensity of the light would be so much diminished as to enable the observer to see the spectrum of the incandescent gases. The difficulty of obtaining a spectroscope of sufficient power, and other causes, prevented the realization of this ingenious idea until October 20, 1868; but in a short letter of this date, received by the secretary of the Royal Society on October 21 (*Proc. Roy. Soc.* xvii. 91), Mr. Lockyer says that he had perfectly succeeded in obtaining and observing part of the spectrum of a solar prominence. He established the existence of three bright lines in the following positions:—1, a red line absolutely coincident with C; 2, a green line nearly coincident with F; and 3, a yellow line near D. The last was more refrangible than the more refrangible of the two darkest D lines by eight or nine degrees of Kirchhoff's scale.

The application of this method of observation had, however, been previously made by Janssen. This astronomer had observed the eclipse of August 18 in India, and the following day he succeeded by means of a powerful spectroscope in seeing the spectrum of a prominence. The account of this observation was sent to the Academy of Sciences in Paris, and arrived and was read on the same day as Mr. Lockyer's description of his later observation of October 20: this is perhaps one of the most curious coincidences presented by the annals of modern science, in which two investigators have published the same result at the same time, though working independently, one in England and the other in India. An account of Mr. Janssen's research was published in a letter to Mr. Warren de la Rue, and printed in the *Proc. Roy. Soc.* 1869, xvii. 276.

It may be well to describe in this place the construction of the apparatus employed by Mr. Lockyer for the investigation of the spectrum of the solar prominences (*Phil. Trans.* 1869, 425). An equatorial telescope of 6 inches aperture, and 9 feet focal length, is used to condense the light of the sun. From the telescope the eyepiece is removed and a strong support adapted to the

tube of the telescope; this support carries a spectroscope containing seven prisms, the slit at the end of the collimator of the spectroscope being placed in the primary focus of the object glass of the telescope so that an image of the sun nearly an inch in diameter is thrown on the slit. By moving the telescope, so as to alter the position of the image, the observer is enabled to examine the light emanating from any portion of the sun, and to place the slit radially or tangentially to the image of the disk. The refraction produced by the seven prisms is so great that the beam of light is deflected through about 270°, so that the observing telescope of the spectroscope is nearly at right angles to the direction of the collimator. When the slit is placed radially to the disk of the sun, so that the edge of the disk is projected on a portion of the slit, a continuous spectrum with black Fraunhofer's lines is seen on looking through the telescope of the spectroscope, and if the atmospheric conditions are very favourable, and there is no haze perceptible round the sun, the spectrum of the sky will scarcely be visible. If it should happen that the image of a prominence falls on the slit the bright lines of its spectrum will be seen as the prolongations of the black lines in the spectrum of the sun's limb. In this manner Mr. Lockyer has shown that the sun is surrounded in every part by a luminous envelope about 800 miles in depth, which he calls the *chromosphere*, and of which the prominences or red flames are merely elevated portions. The bright lines constituting the spectrum of the chromosphere indicate that this gaseous envelope consists principally of hydrogen, the most prominent lines being a red one corresponding to the black line C, a green line corresponding to F, a blue one corresponding to a black line near G, and a violet one corresponding with *h*.

By this mode of observation it is obvious that it is only possible to obtain sections, so to speak, of the prominences, but by moving the telescope to a small extent, so as to bring the different parts of the image of the prominence on to the slit, the observer is enabled to obtain valuable information as to the actual form of the protuberance under examination. It was evidently desirable to be able to obtain an actual view of the red flames, and this was accomplished by Mr. Huggins by placing a piece of ruby glass over the slit of the spectroscope in order to absorb the more refrangible rays, and on now opening the slit of the spectroscope to a sufficient extent, the prominence itself was seen. (*Proc. Roy. Soc.* 1868, xvii. 302.) Mr. Lockyer afterwards found that the red glass might be dispensed with, and that by so placing the telescope that the image of the limb of the sun only just touched the end of the slit when the latter was placed radially, or just touched the edge when it was arranged tangentially, the slit might be safely opened so as to give a beautiful red image of the prominence, and without any apprehension of injury to the eye by the brilliancy of the light. The same fact was independently discovered by Capt. Herschel. The red flames are sometimes of prodigious height; the one observed by Mr. Lockyer on October 20, subtended an angle of 3′ or was about 80,000 miles high. The protuberances are undergoing constant and rapid motion, and by the help of the mode of observation above described, the astronomer is able to watch the alterations of the form of these strange phenomena as easily as those of the clouds in the terrestrial atmosphere. At 11.5 A.M., on March 14, 1869, Mr. Lockyer made a sketch of a protuberance 27,000 miles in height, and consisting of an irregular-shaped cloud and a long perfectly straight one. At 11.15 the straight portion had entirely disappeared, having been apparently absorbed by the irregular cloud.

Mr. C. A. Young afterwards described in the *Boston Journal of Chemistry* a still more wonderful exhibition of solar prominences. (*Nature*, 1871, iv. 488.) At 12.30 on September 7, 1871, Mr. Young saw a prominence about 54,000 miles high, and 100,000 miles long, made up of filaments

mostly horizontal, and floating above the sun, with its lower surface about 15,000 miles above the chromosphere and connected to it by vertical columns. On again examining the protuberance at 12.55, the whole had been completely blown to shreds; instead of the vertical pillars, masses of detached filaments were now seen 100,000 miles above the sun, and rapidly ascending. In ten minutes the highest portions of the masses were no less than 200,000 miles from the surface of the sun, having travelled upwards at the rate of 156 miles per second. The cloud then rapidly disappeared as it cooled, and at 1.15 scarcely anything was left to indicate where this violent action or explosion took place.

The shape of the lines of the spectrum of a prominence is a matter of considerable interest, and one that gives important information respecting the condition of the solar atmosphere. When the spectrum is examined with a narrow slit the red hydrogen line is seen to rest on the black absorption line of the limb of the sun; the base of this line is a little, but not much thicker than the black line; as the distance from the sun increases, the line generally becomes thinner and thinner until it disappears (fig. 86 *a*). The case is very different with the green line corresponding to F; this is often pointed at the end, but on approaching the sun it becomes broader and broader until at the place where it rests on the edge of the solar spectrum it has widened out like the mouth of a trumpet to five or six times the breadth of the black line, which usually is pointed, and disappears in the base of the bright line (fig. 86 *b*). This thickening of the line is due to pressure (109), for as the edge of the sun is approached the chromosphere becomes more and more dense, exactly as is the case with the atmosphere of the earth. In cases where violent action is going on in a prominence, the green line is thickened at various points above the surface of the sun, indicating regions of greater pressure (fig. 86 *c*).

FIG. 86 *a*.

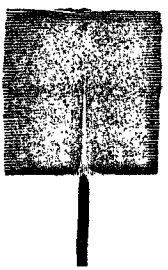


FIG. 86 *b*.

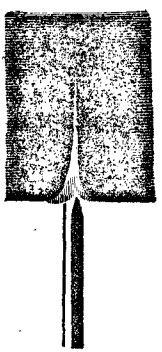
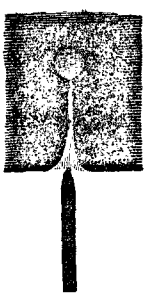


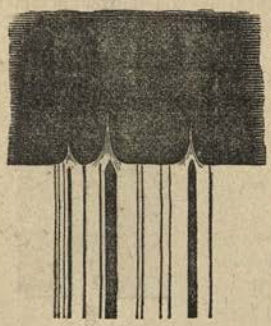
FIG. 86 *c*.



Besides these lines known to be due to hydrogen there is one in the yellow a little more refrangible than the more refrangible of the D lines, and probably the one noticed by Captain Herschel during the eclipse of August, 1868, and which he thought was due to sodium. This line is almost invariably present in the spectrum of the prominences, and was believed by Lockyer to be due to hydrogen; but after numerous trials under very various conditions, Frankland and Lockyer were unable to obtain the faintest indication of it in the spectrum of hydrogen. Mr. Lockyer has since observed that, though generally present in the spectrum of the prominences, the line exhibits certain peculiarities indicating that it is not one of those of the hydrogen spectrum. It appears to belong to an element with a vapour density even less than that of hydrogen, and one which has not hitherto been recognised by chemists among the constituents of the surface of the earth; sometimes, but very rarely, an absorption line corresponding to the bright one is seen in the solar spectrum. Occasionally, during periods of intense action on the sun, the vapours of other elements are projected into the chromosphere; on one occasion, on the 17th of April, 1870, Mr. Lockyer saw *hundreds* of the Fraun-

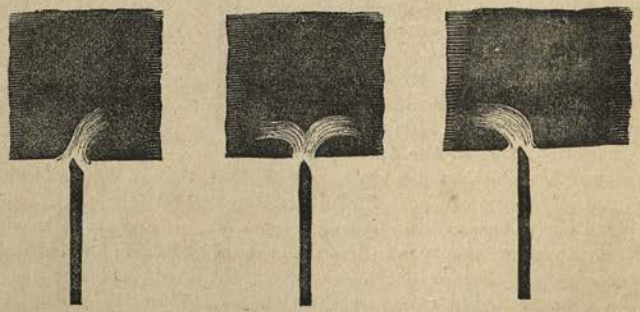
hofer lines beautifully bright at the base of a prominence. The vapours of the elements producing these appearances are only projected to a short distance above the photosphere, and very seldom indeed are seen in clouds floating above the chromosphere. Mr. Lockyer has recognised the spectra of the following metals exhibiting bright lines, sodium, barium, magnesium, iron. One of the most curious points connected with these bright spectra is that only some of the lines are thus seen; and of these, some are longer than others; thus, in the group known as *b*, of which three of the lines are due to magnesium, b_1 and b_2 are of equal length, while b_4 is much shorter. Fig. 86 *d*. Frankland and Lockyer have, however, shown that on examining the spectrum of magnesium obtained by means of the spark of the induction coil between magnesium poles, placed at a short distance from one another, the three *b* lines in the green extend to unequal distances from the metallic points. Of the 460 lines in the spectrum of iron only a few have been observed in the chromosphere, but this is quite in accordance with the laboratory experiments, in which it was found that some of the lines of hydrogen and nitrogen disappeared when the density was very much reduced, the same effect probably takes place in the case of other bodies, and the low pressure on the surface of the sun is perhaps sufficient to reduce the complicated spectrum of iron to a much more simple one.

FIG. 86 *d*.



One of the most interesting phenomena observed on examining the light emitted by the solar prominences is the change of wave length due to the motion of the incandescent hydrogen. As will be afterwards explained (114), when a luminous object recedes from the observer, the wave length is increased, and consequently the ray becomes less refrangible; on the other hand, when the object approaches the observer, the wave length is diminished and the refrangibility increased. If the rate of motion of the object is not insensibly small in comparison with the velocity of light, the alteration of the refrangibility may be so great as to produce a distinct alteration of the position of the lines in the spectrum. If the motion of the luminous object is in a direction at right angles to a line extending from the object to the observer, of course no change of wave length will

FIG. 86 *e*. FIG. 86 *f*. FIG. 86 *g*.



take place; consequently, on observing the spectrum of the chromosphere, or of a prominence rising from the limb of the sun, the bright lines of the spectrum

stand immediately over the black Fraunhofer's lines; on some occasions Mr. Lockyer has noticed an alteration of wave length when examining the prominences, and on March 14, 1869, he obtained evidence of a cyclone on the sun's limb. At one edge of the prominence the green line was thick and a little less refrangible than the black line F, showing that the hydrogen emitting this light was receding from the earth (fig. 86 *e*). At the centre of the prominence the green line was very thick, and broader at the top than at the base (fig. 86 *f*), and at the other side of the prominence the line was more refrangible than the black line, indicating the approach of the hydrogen towards the earth (fig. 86 *g*). The examination of sun-spots by this method has led to several curious observations. When the image of a spot is allowed to fall on the slit of the spectroscope the solar spectrum is seen with a dark band traversing its whole length from red to violet. This band is *dark*, not *black*, indicating that some light, but very little compared with that given off by the photosphere, is emitted by the spot, and thus showing that the spot is a region of general absorption. But this is not all; at those places where the black Fraunhofer's lines cross the dark band, these lines are frequently thickened—the sodium lines for instance (fig. 86 *h*), though this is not the case with all the lines, as some pass across the dark band without any sensible alteration: this shows us that the spot is not only a region of general but also of selective absorption. We have already seen that Frankland and Lockyer have found that a gas in a very rarefied condition gives a spectrum consisting of thin lines, but as the pressure increases these lines widen out and the spectrum may even become continuous. They have also noticed that when light from an ignited solid, and which exhibits a continuous spectrum is passed through an absorbing medium, the lines are thin when the density of the absorbing medium is low, and thicken as the density is increased. This phenomenon is well seen by placing in front of the slit of the spectroscope a hard glass tube containing a small quantity of sodium, and from which the air has been exhausted before sealing: when the light from an incandescent solid, such as lime ignited by the oxyhydrogen blow-pipe, is passed through the instrument, the sodium lines are often seen superposed on the continuous spectrum, on gently heating the tube the sodium is volatilized and the bright lines are gradually replaced by black ones; as the density of the sodium vapour increases the lines widen out considerably. These experiments show that the sun-spots are regions where the cool absorbing medium has a greater density than that above the photosphere, and this increase of density is due to the fact that the spots are depressions in the photosphere containing cool absorbing vapours. In the neighbourhood of the spots the spectroscope often reveals the presence of prominences containing the same constituents as those on the limb, and frequently the black Fraunhofer lines are completely blotted out and sometimes replaced by bright lines which are visible above the brightness of the underlying photosphere. In some cases the motion of these prominences is indicated by a change of the refrangibility of the lines, and occasionally the gases are being projected with such rapidity from the sun that the bright lines lie on the more refrangible side of the absorption lines (fig. 86 *i*). As the prominences are usually seen in the

FIG. 86 *h*.

FIG. 86 *i*.

FIG. 86 *k*.

FIG. 86 *l*.

FIG. 86 *m*.

neighbourhood of spots, and generally on the preceding edge of them, it would seem that the spots may be caused by the projected gases cooling and returning to the sun and thus increasing the quantity of absorbing medium. Occasionally the motion of the absorbing medium is rendered apparent by the alteration of the position of the black lines (fig. 86 *k*) : when this happens the absorption line appears to thicken, but on one side only; sometimes it is even seen quite double. Figs. 86 *l* and 86 *m*.

The spectra of all the metals seem to contain lines some of which are shorter than others. This difference of length may be observed in several ways and is of great importance. One method is to pass sparks between poles of the metal under examination, and by means of a lense to throw an image of the sparks on to the slit of the spectroscope; it is, however, necessary to vary the interval between the poles when dealing with bodies of different volatilities. On examining a spectrum in this way some lines are found to pass from one pole to the other; these are generally the air lines from the incandescent oxygen and nitrogen between the electrodes. If the poles are too close together some of the metallic lines may extend across the interval, and in the case of yellow sodium lines this is invariably the case, these being the longest lines yet observed: in other cases, however, the lines only extend to a certain distance from the poles, the metal magnesium for example gives seven lines, three of which (those which when reversed in the solar spectrum constitute *b*) are longer than the other four. If the electrodes are enclosed in a tube from which the air can be gradually removed, it is found that as the exhaustion proceeds the shortest line first vanishes; on continuing to abstract the air the spectrum becomes more simple, and may in some cases be reduced to a single line. The lines disappear in a constant order, the shortest lines first vanishing and the longest remaining. When the spectrum of nitrogen is observed at very low pressures it is found to consist of a single line in the green: this is the longest line of nitrogen and it is the one observed by Huggins in the spectra of some of the nebulæ (109 *note*). This simplification of the spectrum may also be effected by the dilution of the metal either by combining it with other metals or with non-metallic elements. Thus the spectra of the metallic chlorides contain only the longest metallic lines, the shorter ones being entirely absent; only the three longest lines of magnesium are seen in the spectrum of its chloride. When the spectra of alloys are examined, it is found that the longest lines of both metals are present, and a small variation of composition causes a lengthening of the lines of the metal, the percentage of which is increased. A quantitative process of assay of alloys of copper and gold by this method has been suggested by Lockyer and Roberts (*Phil. Trans.* 1874, 495). It frequently happens that in the solar spectrum only some of the metallic lines are represented by Fraunhofer's lines; when this is the case it is always the longest lines that are reversed: for instance, only the two long lines of aluminium are found in the spectrum of the sun, the other ten being absent. (Lockyer, *Phil. Trans.* 1873, 253.)

When the electric arc obtained from a powerful battery is passed between metallic electrodes placed in a horizontal position, and the image of the arc is projected by means of a lense on the vertical slit of the spectroscope, the spectrum of a section of the arc is obtained, in which the long lines extend to a greater distance from the centre of the arc than the others. Lockyer has photographed a number of the more refrangible portions of these spectra with great success (*Phil. Trans.* 1874, 479). Fig. 86 *n* shows the long and short lines of manganese from one of these photographs. By placing a shutter before the slit of the instrument exposing only a portion of the slit at one time, a number of photographs of different spectra can be obtained on the same plate, and the most rigid comparisons may thus be made. This process has far

extended the knowledge of the constitution of the sun. (Lockyer, *Phil. Trans.* 1874, 479.)

In fig. 86 *o* the coincidences between some of the Fraunhofer lines and the bright lines of the iron spectrum are

FIG. 86 *n*.

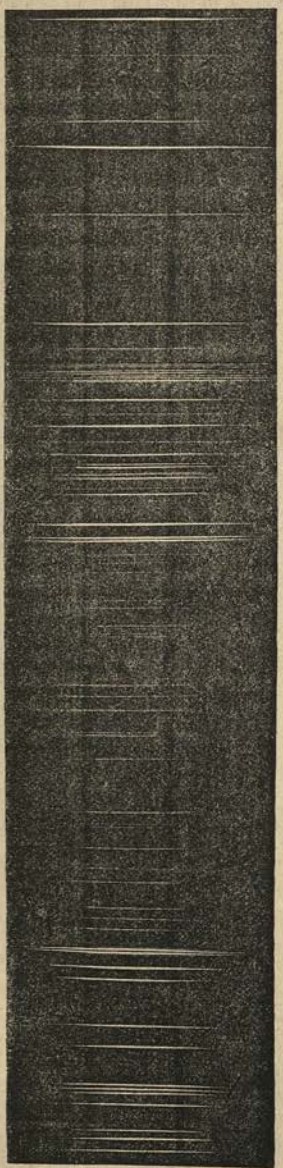
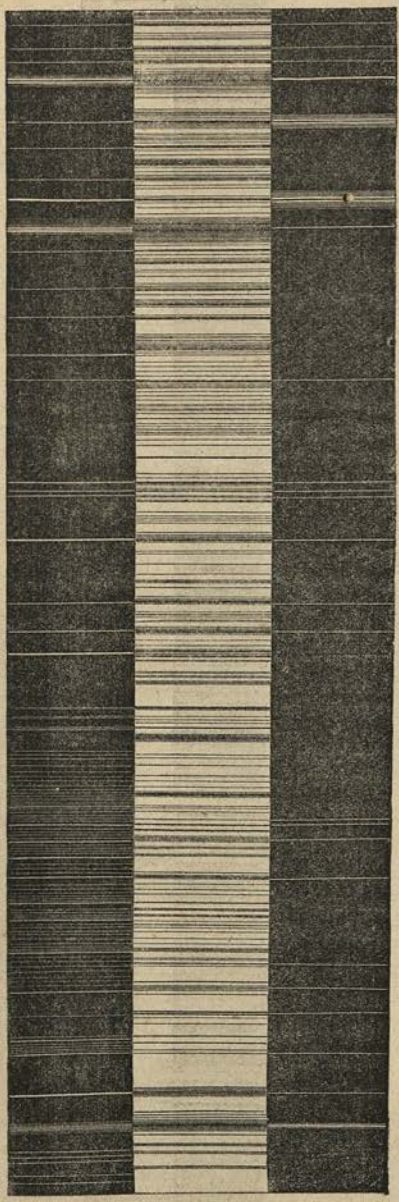


FIG. 86 *o*.

well shown, and fig. 86 *p* is a comparison of the solar spectrum with the spectra of calcium on the left and aluminium on the right. It will be seen that the calcium employed contained aluminium, and the aluminium contained calcium, but the characteristic lines of each metal are evident by their thickness. The H lines in the solar spectrum near the top of the figure are calcium lines, and are coincident with the thick lines in the left hand spectrum, the corresponding lines in the right hand one, where the calcium exists only as an impurity, being thin. The figures are copied from photographs kindly supplied by Mr. Lockyer. In the three preceding figures the upper end is the more refrangible.

FIG. 86 *p*.



(110) *Change in the Refrangibility of Light — Fluorescence.*—A remarkable discovery was made by Stokes, whilst engaged in pursuing the observations of Sir J. Herschel respecting the effect of light upon an acid solution of quinine sulphate. This liquid is colourless when viewed by transmitted light, but if placed in a glass and looked at from above, it exhibits, when exposed to direct light, a beautiful and intense blue upon its front surface; but the light which has passed through one vessel containing the sulphate exhibits no such appearance on the front face of a second vessel of the liquid which is similarly exposed to it. Now the rays which produce this beautiful blue colour are not the ordinary blue rays, but those of the most refrangible portion of the spectrum, which, under ordinary circumstances, are not perceptible to the eye, but which are remarkable for their powerful chemical action,

and show their presence by their chemical effect upon a surface covered with argentic chloride, or with some other photographic preparation.

Stokes (*Phil. Trans.* 1852, 468) found that when a tube filled with an acid solution of quinine sulphate was placed successively in each of the colours of the prismatic spectrum, 'throughout nearly the whole of the visible spectrum the light passed through the fluid as it would have done through so much water, but on arriving nearly at the violet extremity, a ghostlike gleam of pale blue light shot right across the tube. On continuing to move the tube, the blue light at first increased in intensity, and afterwards gradually died away. It did not, however, cease to appear until the tube had been moved far beyond the violet extremity of the spectrum visible on a screen.' On examining by a second prism the dispersed light thus obtained, it was found that it contained rays extending over a considerable range of refrangibility within the limits of the visible spectrum; but the least refrangible rays, or those of the red end of the spectrum, were wanting.

This power of changing the refrangibility is by no means uncommon, especially amongst organic substances, most of which show it in a degree more or less marked. The change is not confined to the invisible rays, but extends also to those already visible, the more refrangible being generally the most affected, though it is not limited to this portion of the spectrum, for with an alcoholic solution of chlorophyll the effect is seen to commence in the red rays. It is, however, to be remarked, that as yet, in every instance, the altered ray gives rise to others which are *less* refrangible. The change is never to rays of greater refrangibility.

Stokes has found (*Journ. Chem. Soc.* 1869 [2], vii. 174) that the fluorescence of an acid solution of sulphate of quinine is destroyed by the addition of the following acids of their salts:—Hydriodic, hydrobromic, hydrochloric, hydroferrocyanic, hydropalladiocyanic, hydroplatinocyanic, hydrosulphocyanic, and hyposulphurous. The introduction of oxacids and their salts produces no effect on the fluorescence.

Amongst the bodies in which this phenomenon is most strikingly exhibited may be mentioned, decoction of the bark of the horse-chestnut (which contains the vegetable principle termed *æsculin*), an alcoholic tincture of chlorophyll (the green colouring matter of leaves), tincture of the seeds of stramonium, and tincture of turmeric. Many of these substances, when spread upon paper, form surfaces which, if used as a screen for receiving the solar spectrum, exhibit a prolongation of the more refrangible end far beyond the violet and lavender rays which are visible on ordinary white paper; and with due precaution the fixed lines of this prolongation may be distinctly seen. A slip of ivory makes a very tolerable screen for this purpose. Glass, coloured yellow with uranic oxide, also exhibits

these phenomena in a very striking and beautiful form, but the material which furnishes the best screen is, according to Stokes, a particular uranic phosphate. (*Phil. Trans.* 1862, 602.)

The light of many artificial flames which are of feeble illuminating power often contains beams fitted to exhibit this kind of reduction in refrangibility in a conspicuous manner. The flame of a common spirit-lamp, and that of burning sulphur, are especially remarkable. If a weak infusion of horse-chestnut bark be poured into a tall jar of water, illuminated by sulphur when burning in oxygen, beautiful waves of phosphorescent light are seen as the two liquids mingle, owing to the scattering of the light rendered visible by the æsculin in solution. In the same way, characters traced with tincture of stramonium on white paper, and nearly invisible in daylight, when exposed to the light of burning sulphur, appear distinctly upon the paper in lines of a pale blue phosphorescent light. The two artificial colouring matters, *fluorescein* and *eosin*, exhibit this property in a remarkable manner, but the effect is most brilliant in the green and blue portions of the spectrum.

The appearance produced by this change in the refrangibility of light is termed *fluorescence*, and bodies which have the power of effecting it are spoken of as *fluorescent* substances. If the incident light be polarized (119 *et seq.*), the dispersed light of the fluorescent body is found to have entirely lost the polarized condition. Hence it seems that the rays which produce fluorescence are first absorbed and then re-radiated, but in a condition of lower refrangibility.

The colour of the fluorescence produced by a substance is constant throughout the spectrum, or nearly so, though at different parts of the spectrum it varies in intensity. Stokes remarks (*Journ. Chem. Soc.* 1864 [2], xvii. 313) that if on examining a solution in a pure spectrum 'we find the fluorescence taking a fresh start *with a different colour*, we may be almost certain that we have to do with a mixture of two different fluorescent substances, the presence of which is thus revealed without any chemical process.'

It has been further ascertained that the nature and intensity of the dispersed light are independent of the state of polarization of the incident rays. The dispersed light is always unpolarized, and appears to be emitted equally in all directions, as though the body were self-luminous.

It is to be noted, even when the exciting rays are homogeneous, that the light emitted after absorption of the exciting rays consists of a mixture of differently coloured rays, without any indication being afforded of the kind of rays by which the fluorescence was excited.

When the fluorescent property of a body is but feeble, Stokes directs the following means to be used for its detection:—Place over an aperture in the shutter of a darkened room a transparent body, which transmits only feebly luminous rays and rays of high refrangibility, and place behind it a second medium which absorbs as completely as possible the rays transmitted by the

first, whilst it transmits those rays which are absorbed by the first. If these media be well chosen, no light will traverse the second screen. Two glass troughs, one filled with the pure solution of ammonio-cupric sulphate, the second with the yellow solution of potassic chromate, will act very well in many cases. Now interpose between the two screens the object the fluorescence of which is to be determined; as soon as this is done, the object, when viewed through the second screen, will appear to be more or less luminous, according to the degree in which it possesses the property in question. (*Phil. Trans.* 1853, 385.)

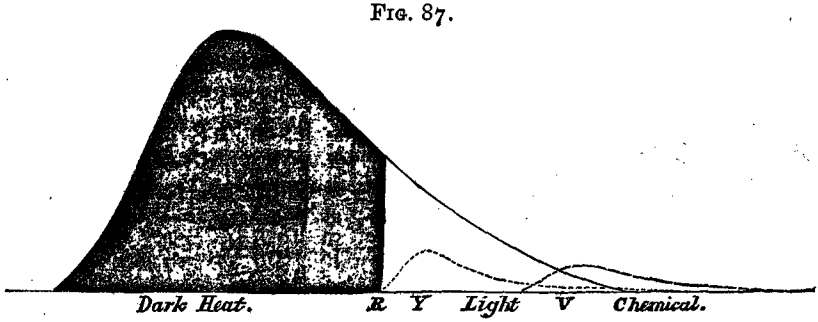
These highly refrangible rays do not pass readily through glass; indeed, most transparent bodies absorb these rays to a greater or less extent. This subject will be again adverted to when speaking of photography (127 *p*). By employing a prism of quartz and lenses of the same material, rays have been found, in the examination of lights from different sources, which extend far beyond the limits of the solar spectrum. The invisible rays in the solar spectrum for example, extend beyond the violet extremity of the spectrum for a distance nearly equal in length to twice that of the luminous portion; but in the electric light obtained by the ignition of charcoal points, the invisible spectrum can be traced nearly six times as far. Each of the metals also furnishes a similar elongated spectrum, when the secondary sparks from an induction coil are transmitted between them. The spectra so obtained are quite characteristic. (W. A. Miller, *Phil. Trans.* 1862, 876; Stokes, *Phil. Trans.* 1862, 599.) By interposing a coloured absorbent medium, such as gaseous chlorous anhydride, in the track of the beam before it is transmitted through the prism, fixed dark lines can be traced at different points through this greatly elongated spectrum.

(111) Prismatic analysis of the solar beam, however, discloses to us other phenomena besides the separation of light into portions of different colours. The radiations from the sun contain not only luminiferous rays, but they are accompanied by a large amount of heat; these rays of heat are susceptible of refraction, like those of light, though as they are for the most part less refrangible than the rays of light, the calorific or heating rays are most abundant near the red end of the spectrum; a large proportion of the rays of heat are less refrangible than any of the rays of light, and fall in the dark space below the red. It has long been well known that light is essential to the health of growing plants, on which it exerts a powerful chemical effect, the more luminous part of the spectrum, according to the experiments of Daubeny and Draper, being the most active in this respect: many metallic and other compounds are also decomposed by rays which occur in greatest abundance in the more refrangible portions in and beyond the blue and violet rays.

In fig. 87 the black unbroken curve will serve to give some idea of the distribution in the solar spectrum of the thermic rays, the maximum intensity of which is beyond the extreme red R, the quantity of heat becoming less and less towards the violet V, beyond which point Müller found it to be nearly imperceptible. The distribution of light is indicated by the dotted line, showing the maximum luminosity in the yellow; while the broken curve shows the chemical effect on compounds of silver, with a maximum in the violet. Upon the undulatory theory it is admitted that the differences between the heating, the luminous, and the chemical rays, are due to differences in the relative wave lengths of the rays, those of greatest wave length being the least refrangible (114). The luminous effect depends upon the peculiar sensitiveness of the retina to rays of a certain wave length; and in like manner the chemical action appears to depend upon the nature of the sensitive substance employed, and its susceptibility to change under the influence of rays usually of high refrangibility and of reduced wave length; each sensitive substance being acted upon by rays of certain wave lengths only.

The annexed diagram will show the relative intensity of the heating, luminous, and chemical rays; the heating effect, as occurring in the different portions of the spectrum, being usually accepted as the measure of the force of radiation at any particular part of the spectrum.

FIG. 87.



(112) *Phosphorogenic Rays.*—The complex nature of the solar spectrum may be further illustrated by its action upon phosphorescent bodies. A certain number of bodies are known which, although they do not, under ordinary circumstances, emit light in the dark, yet, after exposure in the solar rays, continue, without undergoing any perceptible chemical change, to be faintly luminous, after having been removed to a darkened room, for an interval varying from a minute fraction of a second to several

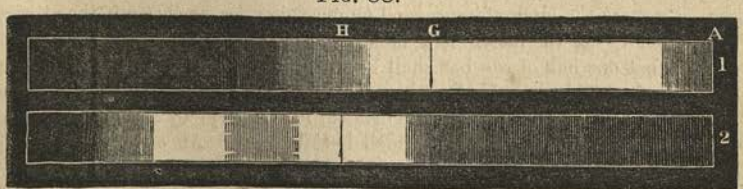
hours. Amongst these substances *Canton's phosphorus*, or impure calcic sulphide, *Baldwin's phosphorus*, or fused calcic nitrate, and *Bologna stone*, which is a barium sulphide, have been long known; but the researches of E. Becquerel (*Ann. Chim. Phys.* 1843 [3], ix. 257, 1859, lv. 5 and [3], lvii. 40) have shown that this property is far more common than was previously supposed, though the duration of the phosphorescent effect is often extremely short. Strontic sulphide, and certain varieties of diamond and of fluor spar, show it strongly; alumina also exhibits it powerfully, though but for a short time, and it is equally marked whether the alumina be crystallized, as in ruby and sapphire, or amorphous, as when recently precipitated. It is worthy of note that silica does not exhibit this property in any of its forms; but the salts of the alkalies, and of the alkaline earths, generally, show it strongly: most other transparent objects, particularly those of organic origin, such as sugar, tartaric acid, and quinine, likewise possess the power, though in a much more feeble degree. Bodies of dark colour, and the metals generally, do not show it.

It has been remarked that all phosphorescent solids lose the power of emitting light when they are brought into solution. Indeed, the liquid form seems to be unfavourable to its display; for solid bodies, such as potassic hydrate and uranic nitrate, which melt at a moderate heat, lose the property whilst fused, but recover it again immediately that they become solid.

Some gases, when enclosed in glass tubes and subjected to the transmission of electric sparks, exhibit a phosphorescence which lasts for a few seconds. Faraday ascribes the luminous tail, which is sometimes observed upon a cloud after the passage of a flash of lightning, to a brief phosphorescence of that portion of the atmosphere which the flash has traversed. According to Morren, pure oxygen, pure nitrogen, and the pure gases generally, do not produce this phenomenon, which he thinks he has traced to the formation of nitric peroxide, N_2O_4. The phosphorescence is most vivid and prolonged if a little SO_3 be added, but other gases, such as sulphurous and carbonic anhydrides, may be substituted, though with inferior effect, for the sulphuric anhydride.

Certain of the phenomena of phosphorescence may be observed by selecting one of those phosphori which retains its luminosity for some time, such as calcic sulphide, and, after it has ceased to emit light in the dark, sprinkling it in powder, over a piece of paper, in a darkened room, and submitting it to the action of the solar spectrum: phosphorescence will be produced in it, but by the more

FIG. 88.



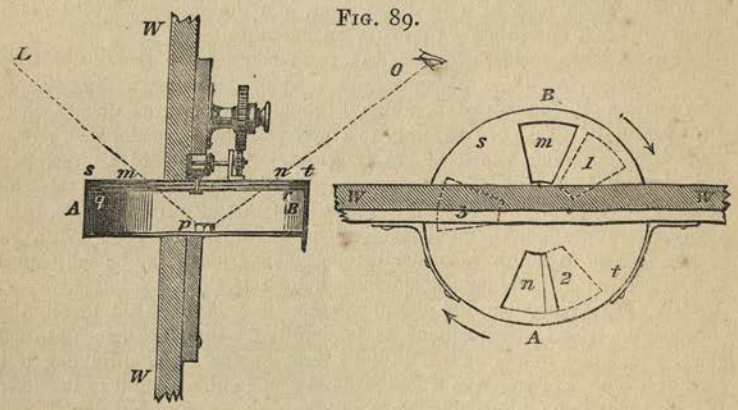
refrangible rays only. There are two maxima of illumination, one of which is within the blue and violet portion of the spectrum; the other is beyond the

termination of the violet. In fig. 88 the stripe 1 represents the diffusion of light in the solar spectrum, whilst 2 gives the relative position of the points of maximum phosphorescence with the calcic sulphide, compared with the luminous spectrum.

The flash of an electric spark, made to pass so that its light shall fall upon a piece of paper thus prepared, is sufficient to render phosphorescent the whole exposed surface of the sulphide: but if the paper be partially covered by a plate of even the most transparent glass, the screened portion will not exhibit any phosphorescence. A screen of rock crystal, however, produces no such absorbent effect, all the portions of the prepared surface being in this latter case equally luminous. The light emitted from charcoal-points ignited by a voltaic current, if it be only instantaneous in duration, is equally unable to penetrate glass so as to produce phosphorescence, although it traverses rock crystal readily. The solar rays, however, traverse either medium equally, without loss of *phosphorogenic* power. A long-continued voltaic light produces a similar result. Glass is only less perfectly permeable than rock crystal to the phosphorogenic rays that accompany the luminous ones. It is interesting to observe that in the phosphorogenic spectrum, inactive spaces occur, corresponding exactly with the position of Fraunhofer's lines, and with the dark bands of the chemical spectrum. (E. Becquerel, *Ann. Chim. Phys.* 1843 [3], ix. 321.)

An ingenious instrument has been devised by E. Becquerel for the purpose of observing phosphorescence of very brief duration. One of the forms of this *phosphoroscope*, as he terms it, is represented both in section and in plan in fig. 89, 1 and 2. It consists of a circular box, A B, of about six inches, or 15 centimetres in diameter, upon the centre of the floor of which the object to be tested,

FIG. 89.



p, is placed; this box is provided with a fixed lid, *s t*, in which are two apertures, *m n*, near the circumference, and on opposite sides, as shown in the plan 2.

In order to use the instrument, it is placed in the shutter, W W, of a darkened room, so that one half of the box shall be within the chamber, and the other half shall project outside it. Under these circumstances, a beam of light, L, may enter the box at *m*, and can be concentrated, if necessary, by a lense, upon the object, *p*, the phosphorescence of which is to be tried. An observer, stationed within the dark room at O, would see this object through the second aperture, *n*. Beneath this fixed lid, however, is placed a second moveable cover, which by means of wheelwork can be made to rotate rapidly in a plane parallel to that of the fixed lid. In this revolving cover are three openings, 1, 2, 3, shown in the

plan. These correspond in size to the fixed apertures, *m n*, but are situated at angular distances of 120° from each other: so that, whenever light is entering by the outer aperture *m*, in the fixed lid, the inner aperture, *n*, is closed; and whenever the object of which the phosphorescence is to be tested is exposed to the observer, no light from without can reach it. Now, if the object be visible to the observer at o, whilst the disk is in rotation, it can only become so by a phosphorescent action; and, by varying the rate of rotation, the interval between the action of the light on the sensitive surface, and the exposure of the object to the eye of the observer, can be made to vary from a period as short as the $\frac{1}{100}$ of a second to any greater interval. Other and still more sensitive forms of the instrument have been employed; but for a description of these the reader is referred to the original memoirs above cited.

The colour of the light emitted by these phosphori is peculiar to each substance, and seldom corresponds with that of the incident ray: it is generally of a lower degree of refrangibility, never of higher refrangibility; for instance, baric sulphide emits a yellow light, though excited by the violet and extra-violet rays: and calcic sulphide, which in different specimens emits an orange, a green, or a blue phosphorescence, is in all cases excited by the more refrangible portion of the spectrum beyond the line G.

The cause of the variation in tint of the phosphorescence produced by different specimens of the same substance, has been minutely examined by Becquerel; and he attributes it to molecular, and not to chemical differences in the phosphori, the results being influenced by the temperature at which the phosphorescent body was prepared, and the crystalline structure and greater or less compactness of the material (*e.g.*, calcic sulphate or carbonate) employed in the preparation of the phosphori. A phosphorescent body, which has been fused, and allowed to solidify again, when placed in the phosphoroscope, often emits light of a tint different from that which it exhibited before it had undergone fusion; for example, plates of crystallized boracic acid furnish a greenish-blue light, but after the acid has been fused the phosphorescence is yellow. Loaf-sugar emits a pale greenish light, but after fusion, on again exposing it in the phosphoroscope, it gives off a much more intense yellowish light.

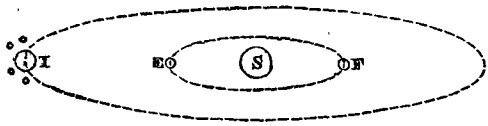
It is to be remarked that, in many cases, the less refrangible rays of the spectrum actually destroy the phosphorescence produced by the more refrangible rays.

Where the phosphorescence has a considerable duration, it is found that elevation of temperature heightens the luminosity, but shortens the duration of the phosphorescence. The effect of heat upon strontic sulphide, when prepared with due precaution, is very remarkable. Certain specimens of it at 0° F. (−18° C.) emit a very beautiful violet phosphorescence; by raising the temperature to 158° (70° C.), the light emitted has a greenish hue, and if the tube which contains the sulphide be heated to about 392° (200° C.) the light becomes of an orange yellow.

Becquerel is of opinion that the phenomena of phosphorescence and those of fluorescence have a common origin—many phosphorescent bodies, such as uranic nitrate, æsculin, and quinine sulphate, emitting light of the same tint as that which they display when fluorescent. This point, however, requires further investigation, since many bodies which are highly phosphorescent show no signs of fluorescence, and the range of colour in the light emitted by phosphorescent bodies is smaller than in the same bodies when they become fluorescent.

(113) *Velocity of Light.*—It is certain that light is the result of a series of progressive actions, since it requires time for its propagation. This was first noticed by Roemer, in 1675 and 1676, who ascertained from observations on the eclipses or *occultations* of the satelites of Jupiter, that when the earth, as represented at F, fig. 90, is situated at its greatest distance from that planet, I, these occultations appear to occur about a quarter of an hour later than they do when the earth is nearest to it, as at E; consequently, between 15 and 16 minutes are required by light in traversing the width, E F, of the earth's orbit, a distance of about 190,000,000 miles.* It has been found by careful observations that the greatest apparent retardation of the eclipses is 16 min. 26·6 sec., or 986·6 sec.: taking the diameter of the earth's orbit as 183,000,000 miles, the velocity of light will be $\frac{183,000,000}{986·6} = 185,481$ miles (298,505,300 metres) per second.

FIG. 90.



In 1849 some experiments were made by Fizeau (*Comptes Rendus*, 1849, xxix. 90), demonstrating that the velocity of light could be determined on the surface of the earth through a distance of only 5·364 miles (8633 metres). For these experiments a telescope was fitted at Suresnes, having at the focus of the object-glass a toothed wheel, the width of the teeth, and of the intervals between them, being equal. When the wheel was rotated an object viewed through the eyepiece was alternately eclipsed and rendered visible for equal spaces of time. By a suitable arrangement a beam of light could be passed along the telescope, issuing from the object-glass in parallel rays. At Montmartre (8633 metres from Suresnes) the light was received on the object-glass of another telescope, the eyepiece of which was replaced by a plane mirror, which reflected the light along its original path, and into the object-glass of the first telescope where it was observed. When the opaque tooth of the wheel was at the focus of the telescope, of course no light issued from the object-glass; but when the tooth was replaced by an interval,

* Or, according to more recent computations of astronomers, 182,000,000 miles (23,573 radii of the earth; Delaunay). When the results of the observations of the transit of Venus on Dec. 9, 1874, have been calculated, an accurate determination of this distance will be obtained.

the light was observed, after traversing a distance of 17,266 metres (10·728 miles). On causing the wheel to rotate rapidly the observer noticed that the light was gradually diminished, and ultimately eclipsed. This happened when the time occupied by the light in travelling from Suresnes to Montmartre and back, was equal to the time necessary for the replacement of the interval between two teeth by the following tooth. On doubling the velocity of rotation of the wheel the light again became visible, the light now passing through one space, and returning through the next. By determining the rate of the rotation of the wheel the velocity of the light was calculated, and found to be 313,274,200 metres (194,663 miles) per second.

These experiments have been repeated by Cornu (*Comptes Rendus*, 1874, lxxix. 1361) with more perfect apparatus, who has found the velocity to be 300,400,000 metres (186,663 miles) a second.

Foucault, by a beautiful application of the revolving mirror, first used by Wheatstone, determined the velocity through the short interval of 20 metres (65·618 feet) to be at the rate of 298,187,000 metres (185,287 miles) a second. The diameter of the earth's orbit may, in fact, be calculated from these terrestrial experiments by multiplying the velocity by the time occupied in the passage of the light across the orbit. This being 986·6 seconds, gives by Cornu's results $186{,}663 \times 986{\cdot}6 = 184{,}162{,}000$ miles. Light would therefore traverse a distance equal to the circumference of the earth in about the eighth part of a second of time.

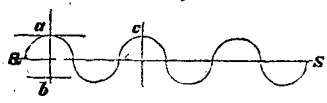
The velocity of light, however, varies with the medium through which it passes; in a more refracting medium its velocity is diminished; but in a medium of uniform density it travels in a uniform direction, and its velocity is also uniform. It may be shown mathematically that if the hypothesis of emission be correct, the velocity must be increased in a more refracting medium, whilst on the undulatory theory it should be diminished; the decision of this question, therefore, affords an *experimentum crucis* between the two theories.

Foucault (*Ann. Chim. Phys.* 1854 [3], xli. 129) has succeeded in solving this important question; by direct measurement he found that light is *retarded* in the more powerfully refracting medium: the relative velocity being inversely as the refractive indices of the media compared. Consequently the theory of emission cannot be longer maintained.

(114) *Length and Frequency of Undulations of Light.*—The

undulatory hypothesis accounts for differences in the intensity of the ray of light R S, fig. 91, by differences in the amplitude or excursion, *a b*, of the undulation; and for the phenomena of colour by differences in the length, *a c*, and in the frequency of the undulations; just as in the phenomena of sound, the pitch of the note is proved to depend upon the number of waves or impulses which occur in a given time: if one note be an octave higher than another note, it will have twice the number of vibrations in the same interval of time; while the length of each wave will be just half that of the waves which produce the lower note: but the extent through which the ear appreciates proportionate differences of rapidity in the undulations which produce sound, is much greater than that which the eye can estimate in the case of light. Most persons can perceive musical sounds in which all possible variety exists between 16 and 2048 vibrations in a second, *i.e.*, including a range of seven octaves, in the highest of which the vibrations are 128 times more numerous than in the lowest. With light the range is much more limited, and extends not quite so far as from 1 to 2.* The average length of a wave of white light is $\frac{1}{50000}$ of an inch, or $0{\cdot}^{mm}000508$, which is nearly equal to the thickness of 6 leaves of gold; but the length of the wave, as well as its frequency, differs in the different colours: in red light it is longer, being about $0{\cdot}^{in}0000299\overline{37}$, or $\frac{1}{33405}$ of an inch, or $0{\cdot}^{mm}000760\overline{4}$, while in violet it is only $0{\cdot}^{in}0000154\overline{84}$, or $\frac{1}{64582}$ of an inch or $0{\cdot}^{mm}000393\overline{3}$ according to the measurements of Angström. The number of vibrations is estimated at five hundred and eighty-six million millions per second (586,000,000,000,000, or 586×10^{12}) in white light; in red light at 392,000,000,000,000, or 392×10^{12}; and in violet light at as much as 764,000,000,000,000, or 764×10^{12}.

Fig. 91.



The length of the waves of light may be varied by motion of the luminous body or the observer towards or away from one another. This may be well illustrated by reference to the corresponding phenomenon observed in the case of sound. This subject was very beautifully described by Professor Stokes in his inaugural address to the British Association at Exeter in 1869:—

'The pitch of a musical note depends, as we know, on the number of vibrations which reach the ear in a given time, such as a second.

* The range in the invisible portion of the spectrum is, however, much greater for the rays which produce fluorescence and chemical action.

Suppose, now, that a body, such as a bell, which is vibrating a given number of times per second, is at the same time moving from the observer, the air being calm. Since the successive pulses of sound travel all with the velocity of sound, but diverge from different centres, namely, the successive points in the bell's path at which the bell was when those pulses were first excited, it is evident that the sound-waves will be somewhat more spread out on the side from which the bell is moving, and more crowded together on the side towards which it is moving, than if the bell had been at rest. Consequently the number of vibrations per second which reach the ear of an observer situated in the former of these directions will be somewhat smaller, and the number which reach an observer situated in the opposite direction somewhat greater, than if the bell had been at rest. Hence to the former the pitch will be somewhat lower, and to the latter somewhat higher, than the natural pitch of the bell. And the same thing will happen if the observer be in motion instead of the bell, or if both be in motion; in fact, the effect depends only on the *relative* motion of the observer and the bell in the direction of a line joining the two,—in other words, on the velocity of recession or approach of the observer and the bell. The effect may be perceived in standing by a railway when a train in which the steam-whistle is sounding passes by at full speed, or better still, if the observer be seated in a train which is simultaneously moving in the opposite direction.'

Dr. Pole (*Nature*, 1875, xi. 232) has calculated the drop of the note of a railway whistle. as observed when an engine passes an observer in another train travelling in the opposite direction. As the trains approach, the note is raised, but, after passing, it will be lowered: the drop is the difference between the two notes:—

Conjoint speed of two meeting trains.		Corresponding drop of the note of the whistle.
Miles per hour	Feet per second	
24	34	A semitone ($\frac{16}{15}$)
45	66	A whole tone ($\frac{9}{8}$)
70	102	A minor third ($\frac{6}{5}$)
85	125	A major third ($\frac{5}{4}$)
108	160	A fourth ($\frac{4}{3}$)
152	224	A fifth ($\frac{3}{2}$)

A similar phenomenon is often strikingly exhibited when the observer is travelling rapidly past the engine of a heavy goods train; on approaching the

engine, the puffs of steam appear to succeed one another rapidly, and on receding, the time between the puffs is appreciably increased, so much so, indeed, that it is difficult to believe that the engine has not suddenly slackened its speed.

Now, since the effects of light are produced by waves caused by the vibrations of the luminous body, it follows that supposing the source of light to be moving towards the observer with a velocity not insensibly small compared with the velocity of light, the light waves will be more crowded together or the wave length will be shortened and the refrangibility increased. Conversely, if the source of light is receding from the observer the waves will be lengthened and the refrangibility diminished. Dr. Huggins found that the spectra of some stars, like that of the sun, contained dark absorption lines, and that the light from Sirius exhibited the two dark lines C and F due to the presence of an absorbing atmosphere containing hydrogen; but in the spectrum of the light from this star the F line did not agree exactly in position with the green line, obtained by passing electric sparks through hydrogen at low pressure, but was a little less refrangible. This increase of the wave length can only be explained by assuming that the earth and Sirius were at the time of the observation receding from one another. The alteration of refrangibility to the observed extent would be caused by a movement of 41·4 miles a second, and of this motion 12 miles a second was attributable to the orbital motion of the earth, leaving 29·4 miles a second as the motion of Sirius from the solar system. (*Phil. Trans.* 1868, 529.) It must be observed, however, that this is not the whole of the motion of the star, for it exhibits an angular movement which obviously would not affect the character of the light.

Dr. Huggins (*Proc. Roy. Soc.* 1872, xx. 386) has since corrected the number obtained for the motion of Sirius, and has calculated the velocity of the movements of several other stars from and towards the sun, with the following results:—

Stars receding from the Sun.	Miles per second.
Sirius	18 to 22
Betelgeux	22
Rigel	15·1
Castor	23 to 28
Regulus	12 to 17
β Ursæ Majoris	17 to 21
γ " "	
δ " "	
ε " "	
ζ " "	

Stars approaching the Sun.	Miles per second.
Arcturus	55
Vega	44 to 54
α Cygni	39
Pollux	49
α Ursæ Majoris	46 to 60

The combination of the observations of the change of refrangibility of light and of the angular motion of stars will doubt-

less be of great service to the astronomer in determining the motion of stars in space.

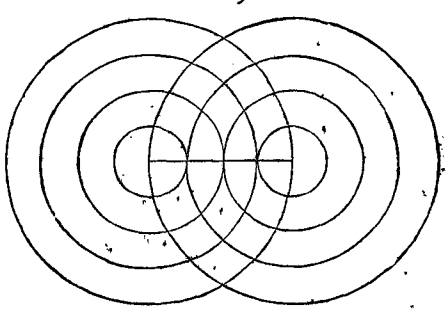
Interference.

(115) *Illustrations of Interference of Undulations.*—One of the simplest, and at the same time most beautiful proofs of the analogy in the mechanism by which sound and light are produced, is exhibited in the phenomena included under the term *interference.*

It is well known that when two stretched strings, not quite in unison with each other, are struck simultaneously, each gives its own note, and the compound sound produced, instead of dying away gradually and uniformly, is subject to a succession of alternate maxima and minima of intensity; the sound alternately dies away and revives several times in succession before it becomes finally inaudible; it thus produces what are termed *beats* in the notes. These beats are due to the interference with each other of the waves produced by the two strings. As one string is vibrating a little faster than the other, it must happen that the direction of the vibrations in the two strings at certain moments must coincide; at this point we have the maximum of sound; the periods of vibration will then gradually recede, and ultimately oppose each other, when they produce a momentary silence.

Again, when two equal impulses are given at a little distance from each other upon the surface of a sheet of still water, each becomes the centre of a system of waves, which ultimately cross each other, and alternately increase and diminish the effect of each other. For example, if in fig. 92 the concentric circles represent two equal systems of waves in water, setting out simultaneously, they will intersect each other; the length of the wave in each system is the same: where the crests of the waves coincide, the elevation will be doubled: but where the crest of one wave coincides with the depression of the other, the water will retain its level surface. These points will occur in regular succession, and form 'lines of double disturbance and no disturbance.' The lines of double disturbance, indicated in the diagram by the points where the circles touch or cut each other, occur at distances

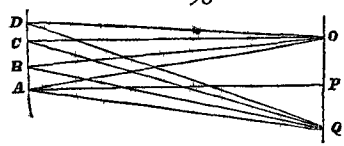
FIG. 92.



which differ by the entire width of one or more waves, or by an *even* number of half waves. The intermediate points, or points of no disturbance, are situated at distances from the centres differing by an *odd* number of half waves: the first will occur at the distance of half a wave; the second at a wave and a half; the third at two waves and a half, and so on. Now these phenomena of undulation in air and in water have an exact counterpart in the case of light.

If a beam of light of a single colour be admitted into a darkened room by two small apertures in a thin sheet of metal, such as pin-holes, placed very near each other, and the light which enters be allowed to fall upon a screen just beyond the point where the outermost rays of the two cones intersect each other,—a spot of increased brightness is seen where the screen is intersected by a line at right angles to it, which line also bisects at right angles the line joining the two pin-holes; on either side of this bright spot will be a series of bands, alternately dark and bright, although the dark bands as well as the bright ones are receiving the rays from both apertures. The addition of light to light has here produced darkness. Let O, Q, fig. 93, represent the two pin-holes, and A B C D, a section of the screen; let P A bisect the distance between the apertures at right angles, and fall vertically on the screen. If the spots A, B, C, D, each represent the centre of a bright band, O A, Q A, will be formed of rays the paths of which are equal; O B, Q B, will differ by the length of one wave; O C, Q C, by two waves; O D, Q D, by three waves; and the black bands between the bright ones will be formed by the interfering of rays, the paths of which differ in length successively by half a wave, a wave and a half, two waves and a half, &c.—(Lloyd's *Lectures on the Wave Theory of Light*, 3rd Edit. 1873, 85.)

FIG. 93.



The length of the paths traversed by the rays from each aperture is equal in the central spot A, and the intensity of the light is therefore increased; but since the path of the rays on either side of this becomes more or less oblique by regular increase or decrease, the lengths of those paths must necessarily be gradually and progressively either augmented or diminished; consequently the number of undulations in each will as gradually be proportionately increased or diminished. When the lengths of the paths of the two rays differ by an even number of half undulations, that is to say, by entire undulations, a bright band is the result; when they differ by an odd number of half undulations, darkness

ensues. Now as the inclination is progressive, there is necessarily a progressive passage from the brightest light to the most complete darkness. By intercepting the light from one aperture, all the dark bands disappear. The measurement of the breadth of one of these bands affords one means of determining the length of a wave of light of that particular colour, if the length of A P be known. Further, since the length of a wave of light differs in lights of different colour and refrangibility, being longest in the red or least refrangible, and shortest in the violet or most refrangible ones, the coloured bands are broadest in the red and narrowest in the violet; and if the experiment illustrated by fig. 93 be performed with *white* light instead of with monochromatic light, the overlapping of the bands of the different colours will produce a succession of iridescent or *coloured* bands, instead of mere alternations of light and darkness.

The phenomenon of interference is one of the fundamental properties of light: indeed it takes place with common light under all circumstances; but the disturbing causes in ordinary cases exactly compensate each other, and it is only by intercepting part of a pencil of rays, so as to remove the compensating system, that the disturbance produced by the remainder becomes manifest; if in the experiment just described the holes are very much enlarged interference will still occur, but the overlapping of the coloured bands will reproduce white light and the interference will be inappreciable. If upon a brilliant plane reflecting surface, such as a polished plate of steel, a number of very fine lines or grooves be traced at equal intervals, so that there may be from 40 to 800 per millimetre, a surface is obtained which reflects a multitude of diverging cones of light, in consequence of the absence of reflection at regular intervals corresponding to the grooves: these cones of rays interfere at their edges without compensation, and a series of colours of the most brilliant tints is perceptible. A variety of natural objects owe the beautiful iridescent play of colours which they exhibit, to a structure of this kind; instances of this occur in the feathers of many birds. The hues of mother of pearl and other shelly structures are also due to their mode of formation in successive extremely thin laminæ, the edges of which form a series of grooves upon their surfaces, and thus produce the phenomenon; impressions of these grooves may often be taken in sealing-wax or in fusible metal, and the same play of colours is then obtained in the impressions.

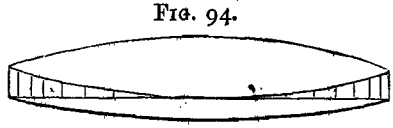
When fine lines are ruled on a transparent plate, such as a

piece of glass, the iridescent colours are observed on looking through the plate at a luminous object. If the luminous object be an illuminated slit placed parallel to the lines on the plate, a series of spectra will be observed, which may be projected on a screen or viewed through a telescope. By measuring the angular distance between the different rays of the spectrum and the distances between the lines on the plate, it is possible to determine the length of the waves producing the coloured rays constituting white light. By a process of this kind, Angström has made the most complete map of the black lines in the solar spectrum, in which the wave lengths are measured to fractions of the ten-millionth part of a millimetre.

(116) *Colours of Thin Plates.*—A different set of colours, also dependent for their origin upon interference, are those termed the colours of *thin plates*. By dipping the mouth of a wine-glass into a solution of soap in water, or what is better still, into gum-water, a bubble may be formed across it; if the glass be laid upon its side, the film becomes gradually thinner and thinner from the action of gravity, and, if viewed by reflected light, a series of iridescent tints is developed, increasing in brilliancy until the bubble becomes reduced to a state of extreme tenuity; it then appears to become black at the thinnest point, and speedily bursts. These colours are due to the interference of a part of the light which is reflected from the second surface of the film, with that which is reflected from the first surface. Any transparent object, such as glass, thin films of metallic oxides, mica, &c., if reduced to laminæ of sufficient thinness, will produce the same effect. The particular colour is dependent on the thickness of the film. In tempering steel, its surface becomes covered with a film of oxide, and the workmen judge of the heat by the colour produced; the higher the temperature which is applied, the thicker does the film become.

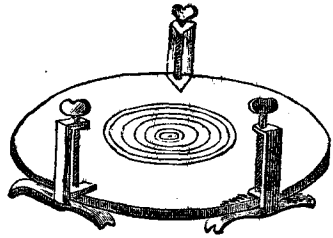
The laws which regulate this phenomenon were traced with great success by Newton. He placed a convex lens, of a very long radius of curvature, upon the flat surface of a plano-convex lens. Fig. 94 shows a section of both lenses, the curvature of which is much exaggerated. Around the point of contact the rings developed themselves with a black spot in the centre, in an order dependent upon the thickness of the film of air included between the two plates (fig. 95). Knowing the convexity of the upper lens, he was able to calculate the thickness of the film required

FIG. 94.



to produce any given tint. He thus found that there is a limit to the thickness of all transparent objects, below which they cease to be visible in reflected light, and another limit in thickness above this, beyond which they reflect only white light: between these two thicknesses the phenomena which we are now considering take place. The thickness of the film which produces any given colour varies with the nature of the reflecting plate, being in the inverse ratio of its refractive index. At and below the thickness of $\frac{1}{2000000}$ of an inch the film of air exhibits a black spot when viewed by reflection, and above $\frac{78}{1000000}$ it reflects white light. In water at $\frac{8}{9}$ of a millionth of an inch a black spot is formed; above $\frac{58}{1000000}$ the reflected light is white. Glass produces the same result at all thicknesses below $\frac{1}{3}$ of a millionth of an inch, and reflects white light at all thicknesses above $\frac{50}{1000000}$ of an inch.

Fig. 95.



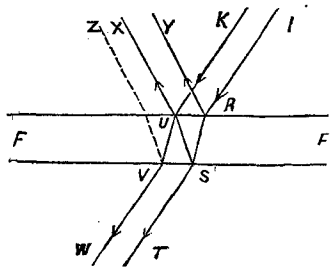
The order of succession of the colours constitutes what is termed *Newton's scale*. Six or seven series of coloured bands may thus be distinctly traced. These rings when produced by homogeneous light are alternately bright and black; the width of the ring is dependent upon the colour, and is greatest in the least refrangible light. The overlapping of the narrow rings by the broader ones in the mixed light of day, is thus, as in the case of the coloured bands produced by interference, the cause of the brilliant succession of colours.

A similar, but fainter series of colours, may be seen in the light that is transmitted through the film, but the tints are in this case complementary to those of the reflected rays. By increasing the obliquity of the incident rays, the breadth of the rings is increased in both transmitted and reflected light. The tints of the transmitted rays are much paler than those seen by reflection in consequence of the large quantity of white light that is transmitted by the glass; they are produced by the interference of a portion of light twice reflected within the plate, with the beam directly transmitted.

In fig. 96, I R represents a beam of light incident upon the film of glass or soap or some substance of greater refractive index than air, shown in magnified section at F F: part of the light, R Y, is reflected; and part, R S T, transmitted; at S, the second surface of the film, a portion of the light is again partially

reflected to U; at U part is transmitted, and interferes with the reflected portion U X, of the beam K U, which falls upon the upper surface of the film at the spot where S U emerges. Now, since the lengths of the paths of the rays, I R S U, and K U differ by a fraction of an undulation, owing to the refraction and reflection of the portion R S U within the film, interference between the two rays is the result, and colours are produced in the reflected beam; in addition to this action, a part, U V W, of the beam, I R, is a second time reflected, and passing out on the lower surface of the film, interferes with the portion of K U, which is directly transmitted, and thus the colours in the transmitted light are occasioned. The dotted line, V Z, represents the track which is taken by the portion of the ray, K U V, which undergoes reflection from the internal lower surface of the film.

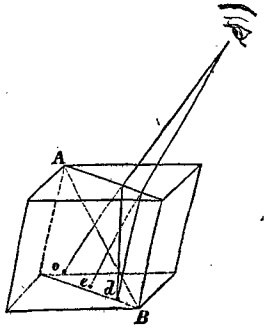
Fig. 96.



§ II. DOUBLE REFRACTION—POLARIZATION.

(117) *Double Refraction.*—The law of refraction (100), which is true for water, for glass, and for other homogeneous uncrystallized media, does not extend to all transparent bodies. In all transparent crystals, excepting those belonging to the regular system, the refracted ray is subdivided into two portions, and hence such bodies are said to possess the property of *double refraction.*

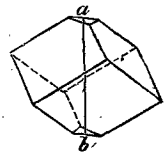
Fig. 97.



This remarkable action upon light is best exhibited in the transparent crystallized variety of calcic carbonate, known as *Iceland spar.* Place upon a dot, *d,* made upon a sheet of white paper, a rhombohedron of Iceland spar, as A B, fig. 97, and look down upon the dot through two of the parallel faces of the rhombohedron, the edges of which, for the sake of simplicity, we will suppose to be all equal; two images, *o, e,* of the dot will be seen instead of a single one; and if the crystal be turned round upon the paper, keeping the eye steadily fixed, one of the images will appear to rotate round the other, which preserves its fixed position. When the eye is placed above the crystal so that

the line between the fixed image and the eye cuts the face of the crystal at right angles, then the line which joins the two images of the dot is, under all circumstances, parallel to the diagonal, A, B, connecting the two obtuse angles of the crystal: around this line the different parts of the crystal are symmetrically arranged. Upon varying the obliquity of the incident ray upon the surface, it is found that the refracted ray which was stationary during the movement of rotation, preserves the constant ratio of the sines, and, as in ordinary cases of refraction, falls always in the plane of the incident ray; whilst in the other ray the ratio of the sines varies at different obliquities of the incident ray; and, excepting in the two positions of the crystal, in which the diagonal joining the obtuse angles is in the plane of incidence, this refracted ray never occurs in this plane. One of the refracted rays follows the usual laws of refraction, and is hence termed the *ordinary* ray; while the other follows a different law, and is called the *extraordinary* ray. There is one remarkable direction in the crystal, in which this double refraction does not take place,—a direction parallel to the line which connects the two obtuse angles of the rhombohedron; this line is called the *optic axis* of the crystal. To render this obvious, a slice of the mineral may be cut in a direction perpendicular to the optic axis, *a*, *b*, fig. 98: it will be found on looking at a minute object perpendicularly through such a plate, that only a single image of it will be seen. When the object is viewed obliquely through the plate, a double image of it will be visible. The separation of the two images increases with the obliquity of the incident light to the optic axis, until it is at right angles to it when it attains its maximum. The point at which the difference between the two rays attains its maximum is selected for determining the index of refraction for the extraordinary ray. In the case of Iceland spar, the extraordinary ray is refracted less than the ordinary ray, the index of the extraordinary ray of yellow light being 1·486, that of the ordinary ray 1·658; such crystals are termed *negative* doubly refracting crystals. Instances, however, are not wanting in which the extraordinary ray is more refracted of the two, as in quartz and ice; the index of the extraordinary ray in quartz is 1·553, whilst that of the ordinary ray is 1·544 (Rudberg, *Pogg. Ann.* 1828, xiv. 45). Such crystals are said to be *positive* or *attractive*.

FIG. 98.



It has already been stated (113) that the velocity of light in bodies is inversely proportional to their refractive indices, con-

sequently in negative crystals the ordinary ray which is the more refracted passes through the crystal with a lower velocity than the extraordinary ray: in the case of Iceland spar, the velocities of the ordinary and extraordinary rays are as 1·486 to 1·658. In positive crystals, in which the extraordinary ray is more refracted than the ordinary, the latter traverses the crystal with the greater velocity: in quartz, the velocities of the ordinary and extraordinary rays are in the proportion of 1·553 to 1·544.

Both rays, if they emerge from a surface parallel to the one at which the incident ray entered, are parallel to each other; but if the surface be inclined, both rays proceed with increasing divergence, each exhibiting the colours of the prismatic spectrum. In all cases, the thicker the crystal the greater is the separation of the two images.

(118) *Influence of Crystalline form on Double Refraction.*—Crystallized substances may be divided into two classes, according to their action upon light; and their optical properties are intimately related to their crystalline form. Thus we have—

1. Singly refracting crystals:—These all belong to the regular system.

2. Doubly refracting crystals:—These may be further divided into two sub-classes. *a.* The *first* sub-class, like Iceland spar, presents only one optic axis in which no double refraction occurs, and it includes all crystals of the rhombohedral and pyramidal systems; such crystals are termed *uniaxal.* *b.* The *second,* of which aragonite and nitre are examples, comprises all crystals of the three remaining systems,—namely, the prismatic, the oblique, and the doubly oblique systems; they have two optic axes, which, however, do not coincide with any of the crystalline axes. Such crystals are said to be *biaxal.*

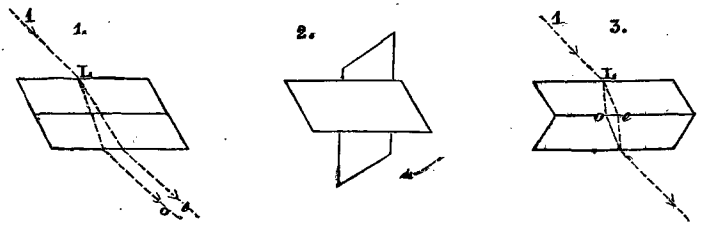
In biaxal crystals, both the doubly refracted rays obey extraordinary laws of refraction.

(119) *Polarization.*—Light that has been transmitted through a doubly refracting prism, has undergone a remarkable modification. If received upon a second crystal of Iceland spar of equal thickness, placed in a position similar to that of the first (fig. 99, 1), both rays pass through it unchanged, except that they are separated further from each other in proportion to the thickness of the crystal, but the extraordinary ray will still be refracted extraordinarily, and the ordinary ray ordinarily; the *principal sections**

* In uniaxal crystals a *principal section* is, in optical language, a plane containing the optic axis and the transmitted ray.

of the two crystals are parallel. On causing the second plate to describe a quarter of a revolution, as shown at 2, still but two

FIG. 99.



images will be seen; but now, the ordinary ray is refracted extraordinarily, the extraordinary ray is refracted ordinarily. When the second crystal describes another quarter of a revolution as at 3, only one image is visible, the rays separated by the first are reunited by the second; in all other intermediate positions, each ray is doubly refracted, and four images become visible: the intensity of the images taken together is constant, one pair fading as the other increases in brightness, and *vice versâ*. Each ray, therefore, on emerging from a crystal of calcareous spar, has acquired new properties: it is no longer subject to further subdivision by a second crystal when placed in particular positions. The rays in fact appear to have acquired sides, and to have new relations to certain planes within the crystal; such rays are said to be *polarized*.

Tourmaline is a doubly refracting prismatic crystal, which, when cut parallel to the axis and sufficiently thick, transmits the extraordinary ray alone, and absorbs the ordinary ray. If a plate of this mineral cut from a brown or green specimen, parallel to the axis of the prism, *a a*, (fig. 100, 1), be placed between the eye and a lighted candle, a considerable portion of light will traverse the plate, and the amount of light will be in no way affected on turning the plate round in its own plane; but if light which has been thus transmitted through one plate of this mineral, be allowed to fall upon a second similar plate, it will traverse this without interruption only when the axes of the two plates are parallel (fig. 100, 1); but it will be completely interrupted where the plates overlap, when the second

FIG. 100.

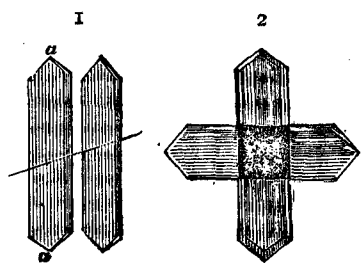


plate is made to describe a quarter of a rotation in its own plane, 2; the axes of the two plates are then at right angles to each other: in all intermediate positions, light will be transmitted with greater or with less intensity, according as the axes are more nearly parallel, or perpendicular to each other.*

If the two beams emerging from a rhombohedron of Iceland spar be examined by means of a plate of tourmaline, it will be found that the ordinary image is most intense when the axis of the tourmaline is at right angles to the principal section of the rhombohedron, and that it is extinguished when the axis of the tourmaline is parallel to the principal section, whilst the opposite results occur with the extraordinary ray. Both rays are therefore polarized, but under different circumstances.

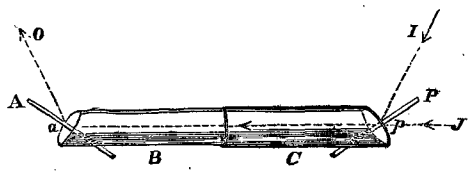
(120) *Polarization by Reflection.*—Polarization may also be effected by means of reflection. Whenever light is reflected from the surface of a transparent medium, a certain portion of such light undergoes this remarkable change; and at a particular angle, varying with each medium according to its refractive index, the whole of the incident light that is reflected is polarized. This effect takes place when the reflected and the refracted ray are at right angles to each other: consequently the greater the refractive index the greater is the polarizing angle: with crown glass this angle is $56° 45'$, with water $53° 11'$, and with Iceland spar $58° 51'$.

When light which has been polarized by any of these means is examined by a reflecting plate, inclined to the ray at the polarizing angle, other remarkable properties are observed. Common light will be reflected indifferently, whether the reflecting plate be placed above or below the ray, to the right or to the left of it, though the inclination of the plate to the ray continue to be the same. It is not so with polarized light; suppose a beam thus affected to fall upon any transparent reflector inclined to the ray at the polarizing angle; if the light be completely reflected when the mirror is placed below the ray, it will not be reflected at all, but be wholly transmitted when the plate is placed on either side, and when placed above, it will again be wholly reflected; at intermediate points part will be reflected and the remainder transmitted; the portion which is reflected is greater the more nearly the plane of the second reflection coincides with that of the first,

* When such a plate of tourmaline is rendered incandescent, the light which it emits is partially polarized, but it is polarized in a plane at right angles to that of the polarized beam which it transmits.

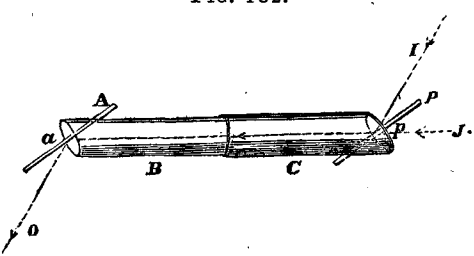
the light being wholly transmitted when the two are at right angles to each other.

FIG. 101.



These facts admit of easy experimental proof. Provide two tubes, B, C (fig. 101), which are fitted so as to allow of their being turned round one within the other. Fasten obliquely to the end of each tube a flat transparent plate of glass, P, A, so as to form an angle of 56° 45′ between the line *p a*, and a perpendicular to the point at which *p a* falls upon the surface of each plate. The tube B, with its attached plate A, can now be turned round on the tube C, without altering the inclination of the plate to a ray passing along the axis of the two tubes; but the plate A, according to its position, will reflect the ray upwards or downwards, to the right or to the left. We can, therefore, alter the plane in which the reflection is produced, without altering the angle of the reflector to the ray. If the light be common light, such as that from a candle placed as at J, no matter whether the plate A be placed below the ray as in fig. 101, or above it as in fig. 102, or to the right or to the left, an observer placed in the direction which the reflected ray, O, would follow, would see the candle distinctly: but the case would be different if the candle were placed as at I, where the light would be reflected from the plate P, along the axis of the tubes; by reflection at this particular angle it would be in great measure polarized. So long as the plate A retains the position represented in fig. 101, the reflected ray would fall in the same plane as that in which polarization took place, and the candle would be seen by an observer stationed in the direction of the reflected ray. But suppose the tube B to be turned slowly round the ray; by following the image as the tube is turned, the light of the candle will be seen to become gradually fainter and fainter, until, when the tube has been turned a quarter of the way round, it will be almost invisible; the plane of reflection is now at right angles to that of polarization, and the light which falls upon A is almost wholly transmitted: on turning it further, the light becomes more and more distinct, till, when the tube has been turned half round, the candle is seen as brightly as at first; the plane of reflection again coincides with that of polarization; if it be turned still further, at the third quadrant the light again disappears, until, on completing the revolution, it is as distinctly visible as at first.

FIG. 102.



The plane of incidence, or the plane of reflection in which the polarization was produced, is called the *plane of polarization*. The original plane of polarization may be easily ascertained in any ray, by whatever means it may have been polarized, because it is always at right angles to the plane in which extinction occurs when the ray is examined by a reflecting glass mirror, inclined to the ray

at the polarizing angle. In this manner it is proved not only that the doubly refracted rays transmitted by Iceland spar are each polarized, but that they are polarized in planes at right angles to each other, the ordinary ray being polarized in the plane of the principal section: in the case of tourmaline, it is found that the emergent ray is polarized in a plane perpendicular to the axis of the crystal.

When the condition of polarization has once been impressed upon a beam of light, it continues to be permanent, whether the subsequent course of the ray be long or short, provided it continue in a homogeneous medium.

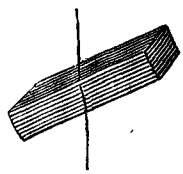
(121) *Distinction between Common and Polarized Light.*— Every beam of *common light* appears to consist of a rapid succession of systems of waves, each system undulating in a determinate plane, always at right angles to the direction pursued by the ray; but the inclination of this plane in one system varies at all possible angles with the plane of vibration in the preceding and succeeding systems. As a resultant of these various motions, common light may be regarded as composed of two beams of light which are vibrating in planes at right angles to each other. *Polarized light* differs from ordinary light in being produced by vibrations in a single plane only, that plane being perpendicular to the plane of polarization; 'and the phenomenon of polarization consists simply of the resolution of the vibrations of common light into two sets, in two rectangular directions, and the subsequent separation of the two systems of waves thus produced' (Lloyd, *Wave Theory of Light*, 3rd Edit. 1873, 169). The effect of a crystal of Iceland spar upon common light will be best understood by considering its action upon a beam which has been already polarized. When a beam of light polarized in any given plane falls upon a crystal of Iceland spar, it is split into two portions, the relative intensity of which varies with the inclination of the plane of polarization to the principal section of the crystal, one beam vanishing altogether when the other is at a maximum. Now common light consists of successive systems of waves, each system being in the condition of a polarized beam; for its vibrations occur in one definite plane. When the undulations belonging to one of these systems fall upon the spar, they are divided into two beams of unequal intensity, but owing to the extremely brief duration of each system, the beams produced by several hundred of these systems in succession are *simultaneously* (so far as the eye can perceive) thrown upon the same spot; the greater intensity of the light produced by some of these systems compensates for

the feebler intensity of others, and the resultant effect is the production of two beams which are of equal intensity whatever be the position of the spar. The result of the analysis is the same as that which would have been yielded by a compound ray, consisting of two other rays polarized in planes at right angles to each other, one plane coinciding with the principal section of the crystal, and the other being at right angles to it.

Since the vibrations of a polarized ray always occur in the same plane, we may, with the assistance of a rude illustration, form some idea of the reason why it appears to be possessed of sides. If we imagine the reflecting surface to be made up of a series of parallel fibres lying only in one direction, these fibres would allow the passage of all the rays in common light which undulate in a plane parallel to their direction, and would reflect the rest: whilst polarized light, if undulating in a plane parallel to the fibres, would be wholly transmitted; but if its undulations were in a plane at right angles to the fibres it would be wholly reflected.

(122) *Polarization by Bundles of Plates.*—Light may also be polarized at other angles by a series of successive reflections from several transparent plates: a pile of glass plates, as shown at fig. 103, is often made use of for this purpose; part of the light is transmitted whatever may be the angle of incidence: but the light polarized by reflection is always equal in quantity to that which is polarized by transmission, and it is polarized in a plane at right angles to it.

FIG. 103.



(123) *Rotation of Plane of Polarization by Analyser.*—In all cases where a polarized beam is received on a reflecting or *analysing* surface, the plane of reflection of which does not coincide with the plane of polarization, the plane of polarization becomes changed. The rotation of the plane of polarization is always towards that of reflection, and the amount of this rotation depends upon the angle of incidence which the ray forms with the analysing plate. If the light be incident upon the analysing plate at the polarizing angle, the plane of polarization is brought to coincide with that of reflection; but the rotation of the plane of polarization is less in proportion as the angle of incidence differs more from the polarizing angle. A corresponding alteration in the plane of polarization is effected by refraction upon the transmitted beam, but it is in an opposite direction.

(124) *Colours of Polarized Light.*—When a beam of polarized light is transmitted in particular directions through plates of doubly refracting bodies, and the light examined by an analyser, a series of splendid phenomena are observed, dependent upon the production of colours, which vary with the circumstances of the

experiment. The simplest method of rendering these colours visible consists in adjusting two reflectors, so that the image polarized by reflection from the first may be extinguished in the second. The first is called the *polarizing*, the second the *analysing plate*: in the above mentioned position the polarizer and analyser are said to be *crossed*. By introducing a thin plate of any doubly refracting substance, such as mica, quartz, or selenite, cut in a direction *parallel* to that of the optic axis, the image suddenly reappears in the analysing plate, but it is tinged of a particular colour. If while the ray falls perpendicularly on the interposed plate, the plate be turned round in its own plane, two positions will occur in which the image completely disappears; these positions are at right angles to each other. In one, the principal section of the plate coincides with the plane of polarization, and in the other it is perpendicular to it. The colour does not change during this rotation, but only varies in intensity. When ordinary unpolarized light traverses such a doubly refracting film, the ray is split into two, the vibrations of which are at right angles to one another; but when polarized light meets with a doubly refracting surface, in such a position that the plane of vibration of the polarized ray coincides with one of the planes of vibration of the crystal, the light is transmitted without change, but the light so transmitted is stopped by the analyser. When the crystal is rotated through 90°, the plane of the polarized ray coincides with the other plane of vibration of the crystal, and the light is stopped by the analyser as before. But if the crystal remain fixed, and the analysing plate be made to rotate, the colour will pass through every grade of the same tint, into the complementary colour, and at each succeeding quadrant the hue is exactly complementary to that which was exhibited in the preceding one. When the polarizer and analyser are parallel, and the plane of vibration of the polarized beam coincides with one of the planes of vibration of the crystal, the light is transmitted without change, and consequently is not stopped by the analyser. The same result is observed when the crystal is rotated 90°: in both these positions the transmitted light is white. In intermediate positions of the crystal a different effect is produced; the polarized ray is then divided into two, vibrating in planes at right angles to one another, and one traversing the crystal at a lower velocity than the other. It will be the simplest to consider, in the first place, the result when the polarizer and analyser are crossed, and the crystal so placed that the planes of vibration of the two transmitted rays make angles of 45° with the plane of

vibration of the polarized ray. Let the line A B. (fig 103 *a*) represent the plane of vibration of a polarized ray traversing a thin film of a doubly refracting crystal at the point *m*, the surface of the crystal being supposed to lie in the plane of the paper: let the intensity of the polarized light, or the amplitude of a wave, be represented by the length *m n*, this ray, in passing through the crystal, will be decomposed into two rays vibrating in the planes E F and G H, and the amplitude of the two component waves will be represented by the lengths *m o* and *m p*. If the thickness of the crystal is such that one of the rays is retarded by one wave length, or any number of whole wave lengths behind the other during the passage of the light through the crystal, on emergence an ether particle at *m* will be moved in the direction *m o*, simultaneously with the motion of another ether molecule in the direction *m p*. When these two rays meet the analyser, the vibration plane of which is indicated by the line C D (fig. 103 *b*), each of the rays vibrating in the planes E F and G H, may be resolved into two vibrations in planes at right angles to one another, one component of each being parallel to the plane A B, and the other to C D. The components parallel to A B cannot be transmitted by the analyser in the crossed position; and although the components *m q* and *m r* are in the plane of the analyser, yet no light is transmitted, as interference takes place. We have seen that an ether particle at *m* will be moved in the direction *m o* simultaneously with the motion of a particle along *m p*; therefore, in the plane C D a particle will move from *m* to *q* simultaneously with the motion of one from *m* to *r*, consequently a particle at *m* will be solicited by two equal and opposite

Fig. 103 *a*.

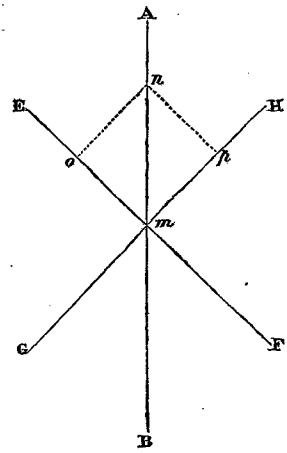
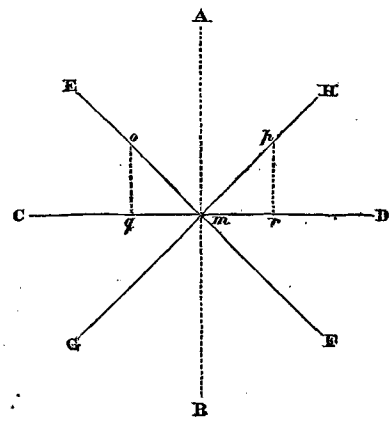


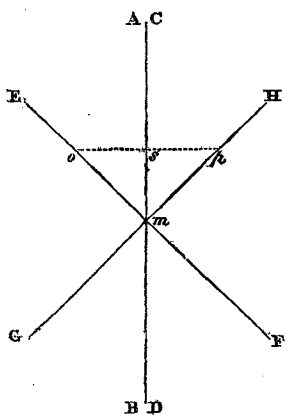
Fig. 103 *b*.



forces, and no motion can result. If the doubly refracting crystal be of such a thickness that one ray is retarded by half a wave length, or an uneven number of half wave lengths behind the other, then, on emergence of the light an ether particle will move from *o* to *m*, at the same time that one moves from *m* to *p*, and in the case of the components in the plane C D a particle will move from *q* to *m* simultaneously with one from *m* to *r*; these being in the same direction will not interfere, but will be transmitted through the analyser. So when the polarizer and analyser are crossed, and the rays transmitted by the crystals differ by a wave length, or whole numbers of wave lengths, no light passes the analyser; whereas, when the rays differ by half a wave length, or an uneven number of half wave lengths, light is transmitted.

In the next place, let us consider the case of the polarizer and analyser being parallel, the crystal remaining in the same position as previously. In fig. 103 *c* the planes of vibration of both polarizer and analyser will be represented by the line A B, and the components of the polarized ray will be represented as before by *m o* and *m p*. If the thickness of the crystal be such that one of the component rays is retarded by one wave length, or a whole number of wave lengths, then, as before, an ether particle will move from *m* to *o* simultaneously with the motion of one from *m* to *p*. These rays meeting with the analyser are each decomposed into two vibrations at right angles to one another, one of each being parallel to C D and the other perpendicular to it. The latter cannot, of course, pass the analyser, whilst the components parallel to C D are each represented by *m s*, and in this case, the vibrations *m o* and *m p* will combine to move a particle at *m* in the direction *m s*, so no interference will take place, and the light will be transmitted by the analyser. If the crystal be of such a thickness that one ray is retarded by half a wave length, or an uneven number of half wave lengths, then a particle will move from *o* to *m* simultaneously with the motion of one from *m* to *p*; the components of those which are parallel to C D will be represented by *m s*, but they are equal and opposite, therefore interference results. So when the polarizer and analyser are parallel, and the rays transmitted by the crystal differ by a wave length, or whole number of wave lengths, no

FIG. 103 *c*.



interference takes place, and light is transmitted by the analyser; whereas, when they differ by half a wave length, or an uneven number of half wave lengths, there is interference, and no light passes.

It will easily be seen (especially by the use of diagrams similar to those above described, and which the student may construct for himself) that the rotation of the analyser or polarizer will cause partial interference; thus in rotating the analyser or polarizer through 90° complete interference will be gradually replaced by no interference, and in continuing the rotation through the next quadrant the interference will increase to a maximum.

What has been stated in the previous paragraphs is obviously only applicable to monochromatic light, or light of one refrangibility or wave length, for interference cannot take place between waves of different lengths. A very instructive experiment may be performed by making two selenite plates, one of which, when yellow sodium light is employed, retards one of the rays an even number of half wave lengths, and the other plate retarding one of the rays an uneven number of half wave lengths. The first, when examined by a polariscope, will appear dark when the field is dark, and light when the field is light, and the second will be bright on a dark field when polarizer and analyser are crossed, and dark on a bright field when they are parallel. When white light is used, complete interference can only ensue with light of one particular wave length, but partial interference takes place with light of the neighbouring refrangibilities. This is readily recognised by examining the light which has passed through the polariscope by means of a spectroscope, when it will be noticed that a band crosses the spectrum which is quite black in the centre, and shaded off towards the edges. The light which leaves the polariscope is therefore complementary to that which is represented by the dark band in the spectrum. The thinnest film will produce interference with the shortest waves, so that the violet is the first to disappear when a piece of selenite in the form of a thin wedge is employed. At places slightly thicker the blue waves will interfere, and so on, through the spectrum. In the first series the rays transmitted by the film differ by half a wave length (or a whole wave length, according to the position of the analyser), so that when examined with white light the extreme end of the wedge will appear nearly white; as the thickness increases the light will appear yellowish brown passing into red; when this happens the maximum interference is in the green; at

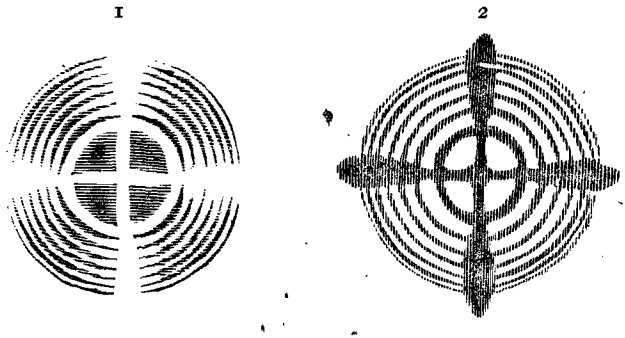
a still thicker part of the wedge the colour will be bluish-green, when the interference takes place in the red. When interference takes place beyond the extreme red end of the spectrum, the light transmitted by the analyser will be nearly white, for since the wave length of the extreme red is about double that of the light of the extreme violet, a piece of selenite, which retards a red ray one half wave length, will retard the blue ray two half wave lengths, there will, therefore, be no interference of the blue rays; on further increasing the thickness, a black band will be observed at the blue end of the spectrum when one ray is retarded three half wave lengths behind the other, and on still increasing the thickness of the selenite this band will travel along the spectrum, but before it has reached the red end a second band appears, which is produced when one of the blue rays is retarded five half wave lengths, the ray of less refrangible light being retarded only three. Further increase of thickness of the crystal will develope more black bands in the spectrum, until ultimately the suppressed light is so equally distributed over the spectrum that the remaining light, when combined, appears white. The thinnest plate of selenite that transmits red light when the polarizer and analyser are crossed (that is, when there is interference in the green part of the spectrum), is about four hundredths of a millimetre, and in the spectrum of the light transmitted there is one black band in the green; a plate of the thickness of three quarters of a millimetre transmits white light in all positions of the analyser, but when polarizer and analyser are crossed or parallel, six or seven black bands appear in the spectrum, the transmitted white light is therefore composed of the remainder of the spectrum. The succession of tints caused by increasing the thickness of the wedge follows the same order as the colours of Newton's rings.

That the colour, when the polarizer and analyser are crossed, is complementary to that observed when they are parallel, is well shown by substituting a rhombohedron of calcareous spar for the analysing plate, so as to obtain two images of the polarized beam: on turning the spar round, the two images will be seen tinged of complementary hues in all parts of the revolution; and if the two images be allowed to overlap a little, the overlapping portions will in all positions be white. The production of these colours is not confined to crystallized minerals, but they are obtainable in a less degree with substances of animal origin, such as quill, horn, or membrane.

(125) *Coloured Rings.*—If the plate interposed between the

polarizing and analysing surfaces be cut from an uniaxal crystal in a direction *perpendicular* to that of the optic axis, the transmitted ray will still be coloured, but the phenomenon is different, and still more beautiful. A series of coloured rings will be observed, intersected by a cross, which, in one position of the analysing plate will be white (fig. 104, 1); on causing the analyser to rotate

FIG. 104.

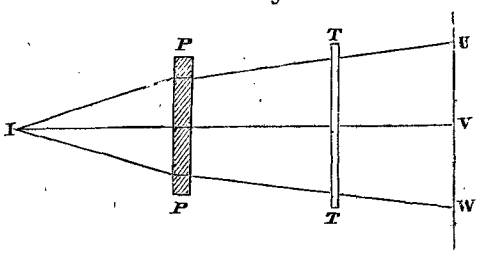


through an arc of 90°, the white cross will be succeeded by a black one (fig. 104, 2), and the rings of colours will exhibit tints complementary to those before observed; at the next quadrant the colours of the first reappear, whilst at the succeeding quadrant they are again complementary. Rotation of the crystal on its own axis produces no change in the tints or in the position of the cross.

The general explanation of these facts is not difficult:—

If P P (fig. 105) be a section of the interposed plate, I the diverging polarized beam, T T the tourmaline, U V W a section of the screen on which the image is received, it is obvious that the rays, I V, which traverse the plate P P, parallel to the optic axis, will suffer no change; but all the lateral rays, I U, I W, which fall upon P P more or less obliquely, according to their distance from the line I V, will be doubly refracted, the two rays being polarized in planes at right angles to one another; one of each these doubly refracted rays will thus be retarded upon the other, and as soon as the two rays are brought into the same plane by the action of the analysing tourmaline, they interfere, and give rise to the brilliant

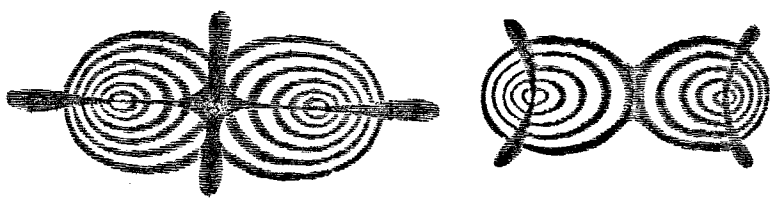
FIG. 105.



colours which are observed. The formation of the cross is occasioned by the absence of any change in the plane of polarization of those rays which traverse the principal section of the crystal which either coincides with the plane of polarization, or is perpendicular to it; these rays, consequently, do not interfere when analysed by the tourmaline. The arms of the cross are alternately white or black according as the axis of the tourmaline is parallel to the original plane of polarization, or is at right angles to it.

With biaxal crystals, such as aragonite, plumbic carbonate, nitre, and borax, the phenomena are even more beautiful, a double system of rings being formed, in which the curves are of a different order, owing to the more complicated phenomena resulting from the mutual action of the optic axes; the surface of the section being oblique to both these axes: the greater the angle formed with each other by the axes, the further will the rings be asunder. The two axes are inclined to each other in nitre at an angle of $5^\circ\ 20'$; in aragonite at an angle of $18^\circ\ 18'$: in borax at an angle of $28^\circ\ 42'$; and in topaz the angle is between 49° and 50°: the position of the intersecting cross varies when the crystalline plate is made to rotate; and the colours become complementary when the analyser is turned round. The general outline of these figures is represented in fig. 106.

FIG. 106.

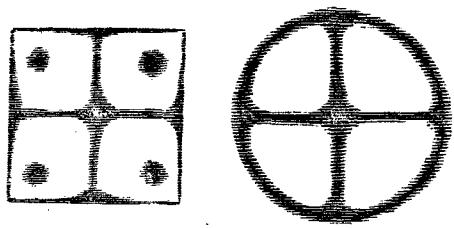


In a plate of quartz cut perpendicularly to the axis the rings are also beautifully shown when examined in the same way; the centre is however brightly coloured, and the crosses only seen at some distance from the centre. When a plate of the same material, but cut parallel to the axis, is examined by monochromatic light, a series of hyperbolic curves is observed, and if the surfaces of the plate make an angle of 45° with the axis of the crystal, the curves are projected as straight lines. With white light the curves are not perceived in consequence of the mixing of the different colours. Two such plates crossed and examined in the polariscope show straight lines even with white light, the centre line being black and the others coloured when the polarizer and analyser are crossed: when they are parallel a

white line is seen in the centre with one dark line at each side and coloured ones beyond. When the planes of vibration of polarizer and analyser are inclined at an angle of 45° the lines disappear. If the vibration planes of the quartz are parallel and perpendicular to that of the polarizer, no lines are seen with any position of the analyser. A combination of two such plates and a plate of tourmaline constitutes Savart's polariscope, an instrument capable of detecting the slightest traces of polarized light. Two plates of Iceland spar or of selenite of suitable thickness exhibit the same phenomenon.

An interesting connexion has been established between the phenomena of coloured lines and rings and the state of molecular elasticity in the solid, by the discovery that these appearances may at will be produced in uncrystallized media, such as glass, or in regular crystals, whenever homogeneity is interfered with in regular progression. This fact is rendered evident by the application of pressure, laterally, to a strip of glass which previously exerted no doubly refracting influence. The parts compressed acquire a negative double refraction; and they are separated, by a neutral line where the particles of the solid retain their normal condition, from those on the opposite edge, which have become dilated, and show positive double refraction. This want of homogeneity exists permanently in glass which has been imperfectly annealed; and, according to the form given to it by grinding, it is possible to alter the elasticity of the particles in different directions, and produce the phenomena of uniaxal or of biaxal crystals; a square or a circular plate, for instance, belongs to the uniaxal system (as shown in fig. 107), while an elliptic plate occasions rings referable to the biaxal form. This fact suggests the probability of the existence of a molecular stress in doubly refracting crystals, and consequently directions in the crystal in which the elasticity of the ether particles differ. The greater the elasticity in a direction parallel to the plane of vibration of the ether particles the more rapid will be the transmission of the ray of light. In bodies exhibiting simple refraction the elasticity is uniform in all directions; in uniaxal positive crystals the axis of minimum elasticity coincides with the optic

Fig. 107.



axis, in negative crystals the axis of maximum elasticity lies in this direction. Biaxal crystals exhibit three axes of unequal elasticity.

(126) *Coloured Rotatory (Circular) Polarization.*—There are, however, cases in which the plane of polarization of the ray is continually changing, during its entire progress through the medium employed to produce the colouration; in some substances the plane of polarization revolves from left to right (like the hands of a clock facing the observer); in others from right to left. Rock crystal was the substance in which this effect was first observed. If a polarized ray be transmitted through a plate of rock crystal cut in a direction perpendicular to that of the axis of the prism, the plane of polarization undergoes rotation in a degree proportioned to the thickness of the plate. The amount of this rotation differs for each colour, and increases according to the increase of the refrangibility of the ray. If the incident light be white, the emerging light, when examined by an analysing plate, is therefore seen to be coloured. The central portion only of the pencil of light (which traverses the plate normally, parallel to its optic axis) exhibits these phenomena; at oblique incidences, the usual law of interference prevails, and coloured rings are formed. Certain crystals of quartz produce left-handed, certain other crystals of it, right-handed polarization. In right-handed quartz the central colours ascend in the scale, when the analyser is turned in the direction of the hands of a watch, the succession being red, orange, yellow, green, &c., and the rings appear to expand with the revolution of the analyser. When homogeneous light is employed, each colour disappears at a particular angle of the analyser. In crystals of quartz of a different hemihedral form, or in which the secondary planes of the crystal are arranged differently from those of the right-handed variety, the same phenomena occur, but in the opposite direction. Sodic chlorate, which crystallizes in forms belonging to the regular system, yields hemihedral crystals, and exhibits a power of rotation over the polarized ray, analogous to that of quartz; the rotation being right-handed or left-handed, according as the crystal is hemihedral to the right or to the left. The terms right- and left-handed rotation refer to the direction in which the plane of polarization has been turned when the observer is facing the instrument with the beam of light passing towards him. Thus, suppose a beam of monochromatic light from a spirit lamp containing a small quantity of sodic chloride to be passing into the polariscope, the analyser

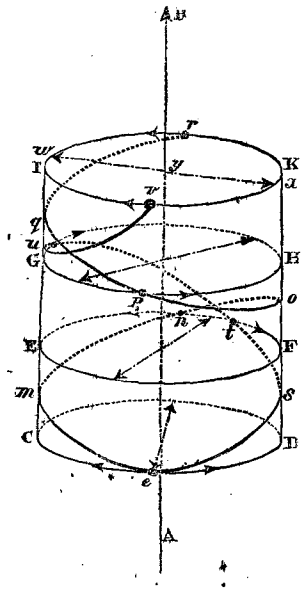
being so placed that the light is not transmitted; if now a piece of right-handed quartz be placed between the polarizer and analyser, the light will be transmitted, and in order to render it again invisible the analyser must be turned to the *right*, that is, in the direction of the hands of a watch facing the observer. If we consider the change with reference to a polarized ray passing from its source through a piece of right-handed quartz, it is clear that the plane of polarization is rotated to the *left*.

When white light is passed into the polariscope in which a plate of right-handed quartz 3 or $4^{mm.}$ in thickness is placed and the light transmitted by the analyser examined by a spectroscope, a dark band will be observed crossing the spectrum. If the analyser be now rotated to the right, the black band will travel along the spectrum from the red towards the violet end. The colour, therefore, which is seen when the eye is applied direct to the analyser consists of a mixture of the colours of the spectrum complementary to that represented by the black band. The passage of the band from the red to the orange, yellow, green, blue, and violet, corresponds to the change of the complementary green to blue, violet, red, orange, and yellow, although it is perhaps inappropriate to apply these names to the different tints which are so complex in their nature.

When a plane polarized ray enters a plate of rock crystal out perpendicularly to the axis, the ray is decomposed into two, but the conditions of the rays are essentially different from those produced when a polarized ray is transmitted into a plate of selenite; whereas in the latter the motions of the ether particles consist of straight lines lying in a plane so that each component ray is plane polarized, in quartz the ether particles move in circles. In one of the component waves the ether particles move in one direction and in the other ray in the opposite; the velocity of rotation of the particles is the same in both rays, but one of them proceeds more rapidly through the crystal than the other. The effect of circular vibrations of this kind is to produce rays of light traversing the crystal in the form of a helix, those particles which move in a right-handed direction producing a left-handed helix. This may be roughly illustrated by placing on a table a vertical cylinder and hanging by it a chain of beads rather longer than the cylinder. If one end of the chain be held in the hand and slowly rotated round the upper edge of the cylinder while the other end rests on the table, each bead will be seen to move round the cylinder in a circular path, while the string of beads will show a helical line: if the rotation

is right-handed (or in the direction of the hands of a clock) the helix will be seen to be left-handed. Let fig. 107 *a* represent a plate of quartz of which the axis is shown by the arrow A B, and let us suppose that plane polarized light is passing upwards through the plate, the plane of vibration being shown by the double headed arrow on the base C D, the ether particles on the circle C D will move in opposite directions, those rotating in the direction *e* D will originate the helical ray *e m n o p q r*, and those moving in the direction *e* C will originate the ray *e s t u v*. It will be seen that the former of these makes one and a half turns round the cylinder, while the latter makes only one turn; the former therefore traverses the crystal more slowly than the latter. Let us now consider the action of these circularly rotating ether particles at the moment of emerging of the helical rays from the crystal on an ether particle *y* in the medium above the crystal. The particle at *r* at a certain moment is moving in the direction *r w*, and at the same instant that at *v* will be moving in the direction *v w*: the result of these two motions will be the movement of *y* towards *w*; it will be readily seen that the effect of the motions of two particles from *x* to *w*, one describing the path *x v w* and the other *x r w*, will be to move a particle from *x* to *w* so as to originate a plane wave, and also that the motion through *w r x* simultaneously with *w v x* will result in a movement in the line *w y x*, consequently on emergence a wave is produced vibrating in the plane *w x*. This plane is however inclined 90° to the original plane of polarization, and on looking down on the cylinder it will be seen that it is turned 90° to the *right*, a result which must follow from the fact that the right-handed helical ray *e s t u v* has passed through the crystal more rapidly than the left-handed ray *e m n o p q r*, which is retarded by half a wave length. If the upper surface of the crystal were at E F, the plane of polarization would be turned 30° to the right, and at G H the plane would be turned 60° to the right. The rotation of the ray is dependent on the wave length of the light and also on the refracting medium producing the rotation.

FIG. 107 *a*.



In quartz the more refrangible rays have their plane of polarization rotated to a greater extent than the less refrangible, and Biot found that the angles of rotation for particular rays are nearly proportional to the squares of the indices of refraction, or, what comes to the same thing, inversely proportional to the squares of the wave lengths. With the knowledge of the wave length at different parts of the spectrum, and the rotation of one of the rays, it is possible to calculate the rotations of the other rays; also the observed rotations multiplied by the square of the wave lengths should give a constant number. The following table in which the angles of rotation produced by a layer of quartz $1^{mm.}$ in thickness, as observed by Broch, and the wave lengths determined by Angström, are employed, and it will be seen that Biot's law is approximately correct: the angle of rotation for the line B is used as the basis for the calculation of the numbers in column 5.

Rays.	Observed rotations.	Wave length $= \lambda$.	λ^2.	Calculated rotations.	Observed rotations.	Observed rotations $\times \lambda^2$.
		m.m.				
B	15°. 18′	·0006867	·0000047156	15°. 18′	15·3°	·0000072148
C	17. 15	·0006562	·0000043060	16. 45	17·25	·0000074278
D_2	21. 40	·0005895	·0000034751	20. 46	21·666	·0000075292
D_1		·0005889	·0000034680	20. 48		·0000075138
E	27. 28	·0005269	·0000027762	25. 59	27·466	·0000076252
F	32. 30	·0004861	·0000023629	30. 32	32·5	·0000076795
G	42. 12	·0004307	·0000018550	38. 54	42·2	·0000078282

The angles of rotation are proportional to the thickness of the quartz, a piece $1^{mm.}$ thick rotating the mean yellow 24°, it follows that a plate $3{\cdot}75^{mm.}$ in thickness will produce a rotation for the same colour of 90°.

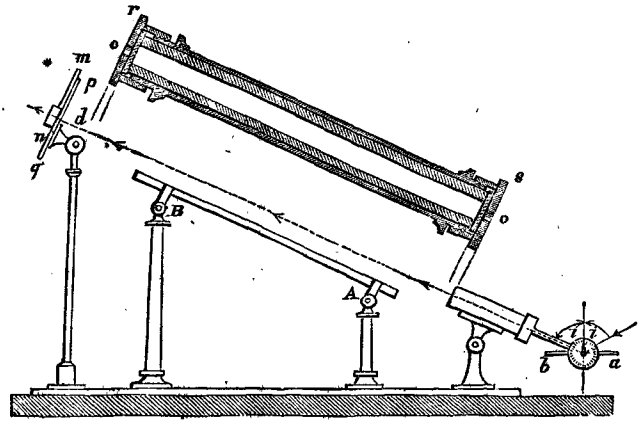
Biot's law does not hold good for all bodies, for in some cases the rotatory dispersion varies very much from that observed in quartz. By an aqueous solution of tartaric acid, for example, the plane of polarization of the green ray is more rotated than that of the violet.

There are many liquids which produce rotatory polarization. Solution of sugar-candy, for example, gives a right-handed rotation; oil of lemons does so likewise. Certain varieties of oil of turpentin produce a left-handed rotation: in some isomeric organic bodies, indeed, the action on polarized light is one of the few important distinguishing properties they possess; hence the value of a proper investigation of their rotatory power when this method is capable of application. In all these cases the degree of the rotation effected by liquids is

much less than that produced by quartz; and, consequently, the light must traverse a much greater depth of the liquid to exhibit the effect. Oil of turpentin has a power not exceeding $\frac{1}{72}$ of that of quartz. In some cases dilution with an inactive liquid does not destroy or even weaken the power, provided that the depth of the column be increased in proportion to the extent of the dilution; this is true with an aqueous solution of sugar when diluted with water. With rotating liquids, such as oil of turpentin, mixture with inactive liquids produces a marked change in the angle of rotation (1555). A mixture of two substances acting oppositely produces a result exactly equal to the difference between the two.

Biot, who discovered the phenomenon of coloured rotatory, or as it is often incorrectly termed, circular polarization,* has applied it to chemical purposes. It may be used, for example, to ascertain the purity of syrups; crystallizable cane-sugar causes a right-handed rotation, while the molasses, or uncrystallizable syrup, produces a rotation of the ray to the left. In order to measure the extent of the rotation, the solution for trial is placed in a long glass tube shown at *o o* (fig. 108), closed at the two ends by flat plates of glass. This tube is placed

FIG. 108.



within a metallic tube, *r s*, for the purpose of excluding stray light. A beam of homogeneous light, obtained by transmission through red glass, is polarized by reflection from the mirror of black glass *a b*. A Nicol's prism,† or other pola-

* Circular polarization was discovered by Fresnel, and is quite distinct from the phenomenon now under consideration.

† The Nicol's prism affords a convenient means of obtaining a polarized beam, depending upon the principle of total reflection (102). It is prepared in the following manner: A long rhomboidal prism of Iceland spar, the base of which is equal to one-third of its length, is divided in half by a plane perpendicular to the plane of the longer diagonal of the base; the line of section

rizing eye-piece, *n*, is so mounted as to admit of rotation around the line *d i*; this eye-piece is provided with a vernier, *m*, which traverses a circle *p q*, divided to degrees, for the purpose of measuring the angular rotation of the eye-piece. The eye-piece is then so adjusted that, when the polarized beam becomes no longer visible, the vernier stands at 0°. Now, if the tube, *o o*, full of solution, be placed on the supports, A, B, so that it shall be traversed by the reflected ray, *i d*, light becomes visible to the observer at *n*, but on causing the eye-piece to rotate to the right or to the left (according to the nature of the solution), the image again disappears: the amount of the movement to the right or to the left expresses the amount of rotatory power exerted by the liquid under the circumstances.

An experienced observer usually substitutes the white light of day for that of the red glass. In this case the rotatory power is measured from a particular violet, the *sensitive* or *transition tint*, the *teinte de passage* of French writers, which, from the suddenness with which by a slight rotation it passes into red on the one side, or into blue on the other, is the most favourable for accurate observation. The tube, with its liquid contents, is interposed between the polarizing mirror and the eye-piece, previously adjusted to zero, and the rotation is estimated by the angular motion necessary to produce the violet tint.* This colour is complementary to the yellow of the spectrum, and is therefore produced when the latter colour is replaced by the black band; as we have seen above, this extinction of the yellow light is effected when the polariscope contains a plate of quartz $3{\cdot}75^{mm.}$ thick, whilst the polarizer and analyser are parallel, for the angle through which the analyser must be turned, in order to stop the yellow light, is 90° from the crossed position.

The most delicate method of employing the sensitive tint in the determination of the rotation produced by a liquid is to place in the instrument a *biquartz*, that is, a combination of two pieces of quartz, one right-handed and the other left-handed, and placed side by side, so that half of the light reaching the eye-piece passes through one and half through the other. If these pieces of quartz are $3{\cdot}75^{mm.}$ thick, they will both show the sensitive tint when polarizer and analyser are parallel. A movement of the analyser to the right will cause the colour of the right-handed quartz to appear red, while that of the left-handed quartz will change to blue. If, therefore, the analyser is so placed that the index points to 0° when the sensitive tint is seen on both halves of the field of view, and a body producing right-handed rotation is introduced, an effect on the colour is produced identical with that which would occur by increasing the thickness of the right-handed and diminishing the thickness of the left-handed quartz—the right-handed would appear blue, showing that the analyser is not sufficiently turned to the right, and the left-handed would be red, showing that the analyser is too much turned to the left. On now rotating the analyser to

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passing through the opposite obtuse solid angles of the prism, so as to divide it obliquely into two equal portions; the two halves of the prism are then re-united by means of Canada balsam. When light is transmitted through the prism parallel to its length, the incident light falls very obliquely upon the layer of Canada balsam; and, as the balsam has a smaller refractive index than the ordinary ray, this ray experiences total reflection, whilst the extraordinary ray alone is transmitted, because, the refractive index of the balsam being greater than that of the extraordinary ray, total reflection does not occur in its case.

* Full details of the most approved method of conducting the operation are given by Clerget, *Ann. Chim. Phys.* 1849 [3], xxvi. 175.

the right, the sensitive tint is reproduced in both halves of the field of view. The angle through which the analyser must be rotated to produce this result is the power which the introduced body possesses of rotating the plane of polarization of yellow light. In Soleil's saccharimeter, which is employed for the determination of the quantity and kind of saccharine bodies present in a solution, the angle of rotation is not directly measured, the effect produced by the sugar solution being neutralized by the alteration of the thickness of a plate of quartz, by the introduction of two wedges of this material between the polarizer and analyser. As a figure and full description of this apparatus are given in Part III. of this work (1555), it will be merely necessary to describe in general terms the principle of the instrument. The light is polarized by means of a doubly refracting or by a Nicol's prism, and then passes through a biquartz, beyond this is placed the tube containing the saccharine liquid, and in front of the tube is a piece of left-handed quartz, followed by two wedges of right-handed quartz. These wedges are attached to slides, moveable in opposite directions by a pinion, so that when the wheel is turned in one direction the narrow ends of the wedges are introduced into the path of the rays, and the combined thickness of the plate increased; reversal of the motion of the pinion diminishes the thickness of the layer. One of the slides holding the wedges is provided with a scale, and the other with a pointer or vernier, and when this arrangement marks 0°, the combined thickness of the two wedges is equal to that of the plate of quartz behind them, which being of opposite rotation, completely neutralizes their action. The eye-piece consists of a small Galilean telescope, focussed to give a clear definition of the division of the biquartz. The polarizer and analyser are so fixed that when the index points to 0°, the transition tint is seen in both parts of the biquartz: on the introduction of a tube containing a rotating liquid, the colours of the two halves of the field change, and must be brought back to their original appearance by a movement of the compensating wedges. The index then shows a number which indicates the increase or diminution of the thickness of the quartz in hundredths of a millimetre, which may be transformed into angles of rotation for any particular colour, by help of the table previously given, indicating the rotation produced by a plate of quartz of the thickness of $1^{mm.}$. For the yellow light from a sodium flame, for example, each division will correspond to a rotation of ·2166°, and for the mean yellow of ·24°. When the sugar solutions are coloured, which not unfrequently happens, the colour of the transition tint is somewhat affected; this difficulty is overcome by placing another Nicol's prism and plate of quartz either between the source of light and the polarizer, or between the analyser and the eye-piece; by turning this combination, the colour of the whole field of view is altered, and the effect of the coloured liquid may be neutralized. Soleil's apparatus can be used only for those liquids which, like sugar solutions, rotate the planes of polarization of the more refrangible rays more powerfully than those of the less refrangible; for other bodies different instruments must be employed.

A convenient instrument is Wild's Polaristrobometer (*Pogg. Ann.* 1864, cxxii. 626, and *Dingler's Pol. Journ.* 1869, cxciv. 338), which depends on the principle of Savart's polariscope, and is more accurate and more easily used than Soleil's saccharimeter. The light entering the instrument is polarized by a Nicol's prism, and then passes into the body of which the rotatory power is to be determined, and afterwards through the Savart's arrangement. In the earlier forms of apparatus, two pieces of quartz $20^{mm.}$ thick were used, cut with their surfaces at 45° to the axis of the crystal, and placed in a crossed position, with their principal sections making angles of 45° with the vibration plane of the analyser, which consists of a second Nicol's prism. In the more recent instruments, two pieces of Iceland spar $3^{mm.}$ thick are employed instead of the quartz. The

analyser is fixed, but the polarizer is attached to a graduated circle, turned by a milled head near the eye-piece, the divisions being read by means of a microscope or by the help of a vernier. In using the instrument, it is most convenient to employ a Bunsen flame coloured yellow by means of a bead of sodic chloride or carbonate, supported on platinum wire. To adjust the apparatus, the graduated circle is turned until the 0° of the scale coincides with the 0° of the vernier, and the polarizing Nicol turned in its socket until the dark lines on the field of view have disappeared, which takes place when the vibration plane of the polarizer coincides with one of the vibration planes of the pieces of Iceland spar. A tube containing the solution to be examined is now introduced, when the dark lines again become visible; by turning the graduated circle until the lines again disappear, the rotation of the yellow ray is at once ascertained. A skilful observer can determine the rotation to one minute of arc.

Jellett (*Proc. Roy. Irish Acad.* 1860, vii. 348) described an analysing prism, which he subsequently (*Proc. Roy. Irish Acad.* 1864, viii. 279) applied to a saccharimeter, the readings of which are very accurate. The analyser is made by cutting a square prism from a rhombohedron of Iceland spar by planes perpendicular to the edges of the crystal, the ends of the prism are then cut at right angles to the sides. On looking longitudinally through such a prism a double image is seen, the line joining the two images being coincident with one of the diagonals of the end of the prism. The prism is now bisected longitudinally by a plane, making with one of the diagonals an angle of 2 or 3 degrees, and the halves are cemented together in a reversed position. On viewing a small circular aperture through the compound prism a disk is seen in the centre consisting of the ordinary beams, and two half disks, separated from the central one, consisting of the two extraordinary beams. The disk in the centre is therefore composed of light, half of which has passed through one side of the prism, the other half having passed through the other side, and polarized in planes inclined to one another at an angle of 4 or 6 degrees; consequently, on examining the light by a Nicol's prism, it will not be possible to quench the light of both halves of the disk simultaneously; when the plane of vibration of the Nicol is equally inclined to the vibration planes of the two halves of the compound prism, the two halves of the disk will be equally illuminated. In the saccharimeter, the liquid to be examined is placed in a tube closed with glass plates, and capable of being raised or lowered in a wider vessel containing oil of turpentin, of a rotation opposite to that of the liquid under examination; the length of the column of turpentin necessary to neutralize the effect of the rotating liquid is measured by a vernier. Cornu (*Bull. Soc. Chim. Paris*, 1870, xiv. 140) has employed Jellett's prism, in conjunction with a Nicol, reading the rotation directly on a graduated circle.

It is remarkable that the vapours of oil of turpentin and of some other liquids which exhibit the power of coloured rotatory polarization, display the phenomenon when seen through very long tubes, though more feebly than the liquids themselves.

Sir Charles Wheatstone has discovered that when a ray of light is polarized by a plate of black glass, transmitted through a film of a crystal of quartz cut parallel to the optic axis, and then reflected from a plate of polished silver at an angle of 18°, it exhibits all the phenomena of circular polarization when examined by means of a Nicol's prism. A plate of quartz cut perpendicularly to the optic axis behaves when examined in this manner as it would when observed with rectilinear polarized light. (*Proc. Roy. Soc.* 1871, xix. 381.)

(127) *Magnetic Polarization.*—Faraday discovered another modification of coloured rotatory polarization, which homogeneous

transparent solids and liquids exert upon light with various degrees of intensity, when subjected to magnetic power of very exalted degree. Some of these singular results will be more particularly described at a future point (322).

§ III. Influence of light on chemical attraction—photography.

(127 *a*) *Supposed Influence of Light on Crystallization.*—It is a familiar observation that bodies which crystallize as they are condensed after spontaneous sublimation,—such as camphor, naphthalin, and Faraday's chloride of carbon,—if placed in glass vessels often collect upon the side of the glass which is exposed to the light, whilst no crystals are deposited upon the other side of the vessels. This effect, however, is not confined to crystallizable substances. If a few drops of water be placed at the bottom of a bottle, the sides of which are kept dry, and the mouth of the bottle be closed, a deposit of globules of moisture will generally be observed upon a particular portion of the side, and often this deposit occurs upon the illuminated side of the bottle. A similar effect is frequently seen in the vacuum of a barometer, globules of mercury being condensed upon the side of the tube. It was generally supposed that these effects were due to some subtle influence exerted by light, but Tomlinson has shown conclusively that they are simply owing to differences in temperature; the crystals, or the liquid, becoming condensed upon that part of the vessel which, from accidental circumstances, is the coldest (*Phil. Mag.* 1862 [4], xxiv. 358).

(127 *b*) *Chemical Actions of Light.*—The rays of the sun are not only the great source both of light and heat to the globe which we inhabit, but they are constantly exerting upon the various substances upon its surface, a chemical influence of the utmost importance to the existence of animal and vegetable life, and to the permanence of the present order of creation. The occurrence of this remarkable chemical activity in the solar rays may be shown in various ways:—When perfectly dry chlorine is mixed in the dark with hydrogen, no chemical change takes place; if the two gases have been exposed separately to the beams of the sun, and have subsequently been mixed in the dark, they may be preserved in this condition also without change, so long as they are screened from the light; but if the mixture be exposed to diffused daylight, it will be observed that the two gases begin gradually to combine, and if they be free from admixture with uncombined oxygen or excess of hydrogen, sudden combination with explosion occurs when they are exposed to the direct rays of the sun. The rapidity with which this combination occurs is proportional to the intensity of the light; and an instrument for measuring the amount of the action which is produced by diffused daylight was described by

Draper, under the somewhat fanciful name of the *tithonometer* (*Phil. Mag.* 1843 [3], xxiii. 402).

(127 *c*) *Photo-chemical Induction.*—An elaborate investigation of the circumstances which influence the action of light upon a mixture of chlorine and hydrogen, by Bunsen and Roscoe, will be found in the *Phil. Trans.* 1857, 355.

From these investigations it appears to be probable that a species of induction precedes the chemical action. It was ascertained by Draper that on exposing the explosive mixture of chlorine and hydrogen to diffused daylight, the amount of condensation gradually increases for a few minutes, until it attains a maximum, at which point the rate of combination between the two gases continues to be constant for equal amounts of incident light. Draper attributed this slow attainment of the maximum rate, to an effect of light upon chlorine alone, in consequence of which it was gradually converted into a new and more active modification. Bunsen and Roscoe, however, did not find that either chlorine or hydrogen, when separately exposed to light, exhibited, after they had been mixed and again exposed, any action different from that observed when the gases were prepared and mixed in the dark and then exposed to light; they consider that the light acts by overcoming certain resistances which oppose the combination of the two gases; and this peculiar action they term *photo-chemical induction.* The time which elapses before the maximum action, due to the light, is attained, varies considerably in different experiments,—ranging from 3 or 4 minutes up to 10 or 15. The more intense the light, the more rapidly is the maximum attained, but the increase is in a greater ratio than the mere increase of light. This inductive influence upon the gases is not permanent. If they are placed in the dark for a short time, and are afterwards again exposed to the light, an interval of exposure similar to the first is required before the maximum rate of combination is attained. Dr. E. Budde (*Phil. Mag.* 1871 [4], xlii. 290) finds that when a differential thermometer containing chlorine gas, instead of air, is exposed to sunlight or to the ultra-violet rays of the spectrum, the gas expands: this he explains by supposing that some of the chlorine molecules are decomposed, free atoms of the element being thus produced, and which would account for the very energetic character of chlorine under the influence of actinic rays.

(127 *d*) *Action of Light on Mixed Gases.*—The presence of foreign gases in the mixture of chlorine and hydrogen greatly

diminishes its sensitiveness to the action of light: the addition, for example, of 3 parts of hydrogen, to 1000 of the mixture reduced the rate of combination for equal amounts of exposure from 100 to 37·8. The effect of oxygen is still greater; 5 parts of oxygen in 1000 of the mixture reduced its sensitiveness under similar exposure, from 100 to 9·7, and 13 parts of oxygen to 2·7. The following table shows the results obtained with these and some other gases,—taking the amount of condensation observed in equal times with the pure mixture of equal measures of chlorine and hydrogen as in all cases equal to 100:—

Rate of Combination for Intervals of Equal Exposure to Light.

Nature of Foreign Gas.	Vol. of Chlorine and Hydrogen.	Vol. of Foreign Gas.	Ratio of Condensation.
None	1000	0	100
Hydrochloric Acid	1000	1·3	100
Chlorine	1000	10	60·2
		75	50·3
		180	41·3
Hydrogen	1000	3	37·8
Oxygen	1000	5	9·7
		13	2·7

Bunsen and Roscoe found that a gas consisting of equal volumes of chlorine and hydrogen could be obtained with certainty, by the electrolysis of a solution of hydrochloric acid of density 1·148, if a sufficient interval were allowed for the liquid to become saturated with the two gases. This gaseous mixture gave perfectly constant results for equal exposure to a light of uniform intensity, provided care was taken to insure the complete expulsion of air from the apparatus. The constant source of light which they employed was that of a jet of coal-gas, burned from a platinum nozzle, and connected with a special apparatus for regulating the efflux of the gas. The colouration of the flame by a trace of foreign matter materially affected its chemical activity.

Chlorine and carbonic oxide gas also enter slowly into combination under the influence of sunshine. Two volumes of chlorine and two of carbonic oxide in this manner become condensed into two volumes; the result is the formation of the irritating pungent gas known as phosgene gas, in allusion to the mode of its production. It is remarkable that the direct union of these gases cannot be effected by any other means.

Organic chemistry abounds with instances in which combinations and decompositions are effected by chlorine, under the in-

fluence of the solar ray: some remarkable cases of this kind occur in the transformations of Dutch liquid, or ethylenic chloride, produced by chlorine. The operation of bleaching linen, by exposure to moisture and light for several weeks during summer, is another process which illustrates the influence of solar light in the production of chemical changes. But the chemical actions produced by the sun's rays, which are taking place unperceived around us, are of infinitely greater importance than those limited transformations which can be effected in the laboratory or the bleach-field; for it is upon these unobserved, yet daily renewed alterations, that the growth and renovation of the entire vegetable kingdom are dependent. The great chemical effect of light appears to be that of a powerful reducing or deoxidizing agent. Under the influence of solar light, the green parts of plants perform their allotted function in the purification of the atmosphere, by absorbing and removing carbonic anhydride, in virtue of which they fix the carbon in their tissues, and thus supply themselves with food; by a similar decomposition of water they obtain the hydrogen needed for their growth, while they return into the aërial ocean a portion of the oxygen with which the carbon and the hydrogen were previously in combination, and thus assist in maintaining that uniformity in the composition of the atmosphere which is indispensable to the healthful existence of animal life.

If solar light be excluded from plants, none of these decompositions are effected; the carbonic anhydride escapes unchanged into the air, and no fixation of carbon ensues; the plant becomes pale and succulent, whilst its functions languish. Gardeners take advantage of this knowledge in order to procure vegetables of more delicate flavour; by earthing up the plant, as is practised with celery, or by covering it with a tile, as in the case of endive, or by enclosing it in a bell-jar, as is usual with seakale, the light is more or less excluded, and the bleaching which is desired in vegetables for the table is produced.

(127 *e*) *Reducing Influence of Light on Metallic Salts.*—Much attention has been given to the study of the chemical actions produced by light, in consequence of the beautiful inventions of the Talbotype and the Daguerreotype. These remarkable processes, as well as others of a somewhat similar character, appear to depend upon the power which the more refrangible rays of the solar spectrum possess of causing the decomposition of the oxide, chloride, or bromide of silver, and of certain compounds of

some other of the metals. This decomposition by means of light, usually takes place under the concurrent influence of hydrogen, or of some metallic body, or other reducing agent, which acts either by setting free the silver or other metal, or by producing a lower oxide, chloride, or other compound of the metal. In other instances, as with argentic iodide, a molecular, and not a chemical change, appears to be produced by exposure to light. In this case there is no immediate change of colour, but it may be rendered visible by the reactions produced by the application of suitable chemical reagents to the compound after it has been so exposed to the solar ray.

The following instances of the effects of light have long been observed by chemists:—If a piece of white silk be dipped into a solution of auric chloride, and exposed whilst in a moist state to the sun's light, the silk becomes first green, then purple, and in less than an hour a film of metallic gold is produced upon its surface. Argentic nitrate in solution in pure water undergoes no change when exposed to the light, but if any organic matter be added to the liquid, a black deposit is gradually formed; and if the salt be placed upon the surface of the skin, upon paper, or upon linen, the well-known blackening effect for which it is valued as a marking ink for linen is produced. Moist argentic chloride retains its dazzling whiteness if preserved in total darkness, but it assumes a violet tint, which gradually deepens in intensity, if exposed even to the diffused light of day,—a portion of chlorine being liberated in the process.

(127 *f*) *Photographic Printing.*—The earliest experiments that have been published upon the production of pictures by the action of light, appear to have been made by Thos. Wedgwood and Davy in the year 1802. Wedgwood moistened white paper, or white leather, with a solution of argentic nitrate (nitrate of silver), and by its means copied paintings on glass, and took profiles; but neither he nor Davy was able to devise any means for preserving those pictures when exposed to diffused light.

The subject attracted but little attention until the commencement of the year 1839, when Fox Talbot made known (*Phil. Mag.* 1839 [3], xiv. 196) his process of *photogenic drawing*, which consisted in soaking ordinary writing-paper in a weak solution of common salt, and when dry, washing it over upon one side with a solution of argentic nitrate, consisting of 1 part of a saturated solution of the nitrate with 6 or 8 parts of water. This operation was performed by candle-light, and the paper was dried at the fire; in this manner a film of argentic chloride, mixed with an excess of argentic nitrate, was formed upon the surface of the paper. Suppose that it were desired to obtain a copy of an engraving, or of the leaf of a tree; one of the sheets so prepared was laid under the engraving or the leaf which was to be copied:

the two were pressed firmly together between two plates of glass, and exposed to the direct rays of the sun, or even to diffused daylight, for a period of half an hour or an hour. The impression thus obtained was a *negative* one, that is to say, the shadows were represented by lights, and the lights by shadows; those portions of the surface which had been exposed to the strongest light becoming dark; in the half tints, where a feebler light had been transmitted, the blackening became less evident; and the parts corresponding to the deep shadows in the engraving remained white. The pictures were fixed by immersing them in a strong solution of common salt. Considerable improvements in detail have been introduced into this process since it was first published, but, in principle, this operation, which has been termed *photographic printing*, remains unchanged.

A very good paper for this kind of printing may be obtained as follows:—Prepare a solution of sodic or ammonic chloride, containing 23 grammes to the litre, or 10 grains of the salt to each ounce of water. If French paper (which is sized with starch) is to be used, it will be improved by dissolving 2 grammes of gelatin in each litre of the solution of salt. Pour this liquid into a flat shallow dish, and having cut the paper into pieces of a convenient size, take a sheet of it by the two opposite corners, and bring it down upon the surface of the solution, so that the middle of the sheet shall be first moistened; then lower it gradually towards each corner, so as to exclude air-bubbles. After the lapse of a minute, it may be removed from the solution, and hung up to dry. In order to render the paper sensitive, prepare a solution of argentic nitrate, containing about 114 grammes to the litre, or 50 grains of nitrate to the ounce, and lay the sheet upon the surface of the solution in the same manner as before; in about three minutes' time the sheet may be removed: it must be raised by one corner with a pair of forceps tipped with sealing-wax, allowed to drain, and hung up to dry. The process of immersion in the silver bath and the drying must be performed in a darkened room.

Another sensitive paper, which is often used, may be prepared by forming a solution which contains 182 grammes of argentic nitrate to the litre, or 80 grains in each ounce of distilled water, and adding caustic ammonia until the precipitated argentic oxide is almost redissolved; the solution should be preserved in a dark place. The paper, having been previously salted, is excited by brushing it over with this solution by means of a pledget of cotton wool. The paper is allowed to dry in the dark, and should be used immediately.

In order to protect the picture obtained upon either of these papers from the further action of light, it is now usual to adopt the method introduced by Sir J. Herschel, which consists in soaking the picture in a concentrated solution of sodic thiosulphate (or hyposulphite of soda, as it is called in commerce) containing about 1 part of the salt to 2 parts of water: this salt combines with the undecomposed salt of silver, and renders it soluble. By washing the picture for 5 or 6 hours in water, which should be frequently changed in order to ensure the thorough removal of the salts of silver and of the thiosulphate, the surface is secured from further change when exposed to light.

(127 *g*) *Talbotype*, or *Calotype Process*.—In 1841, Fox Talbot took out a patent for the very beautiful process to which his name has since been attached.

In this remarkable operation the surface of the sheet of paper is coated with argentic iodide, which is not sensitive *per se* to the action of light if the process of immersion in potassic iodide is the last operation previous to washing. In order to render it sensitive, it is washed over with a mixture of argentic nitrate, with gallic and acetic acids, and then exposed in the camera to the object which is to be copied. After the lapse of a few minutes (the time required varying with the intensity of the light), the paper is withdrawn from the camera. Unless the light has been very strong, no image is visible, or a mere outline only, but the compound has undergone a change of a very singular nature, for if the blank sheet be protected from the light, and washed over with the mixture of argentic nitrate with gallic and acetic acids, on gently warming it, a *negative* image appears with wonderful distinctness and fidelity,—the portions which have been exposed to the strongest lights assuming the darkest tints. The development of the image appears in this process to be due to the reducing agency of the gallic acid, which acts more rapidly upon the argentic nitrate in contact with those portions of the iodide which have been most freely exposed to the action of light. This dormant picture may be developed many hours or even days after it was produced, if the paper be preserved from the light. It seems as though the light, without actually producing a decomposition of the particles of the silver compound upon which it falls, gives to them a particular condition which predisposes them to produce decomposition in a reducible mixture consisting of argentic nitrate and gallic acid. The process may be conducted in the following manner:—

1. *Preparation of the Iodized Paper.*—A sheet of smooth writing paper, such as that manufactured by Turner, of Chafford Mills, of uniform texture, and free from stains and spots, is pinned upon a board by two of its corners, and brushed over uniformly with a solution of argentic nitrate containing 75 grammes to the litre, or 33 grains of the salt in an ounce of distilled water. The solution is best applied by means of a brush consisting of a flock of cotton wool partly drawn through a glass tube, which furnishes a convenient handle: whilst the paper is still moist, it is immersed in a bath of potassic iodide, containing 46 grammes of the iodide to a litre of distilled water, or 20 grains to the ounce, taking care to avoid the occurrence of air-bubbles. In about two minutes, or as soon as the paper has acquired a uniform yellow colour throughout, it is transferred to a vessel of water, where it is allowed to soak for two or three hours, changing the water three or four times, so as to remove all the soluble salts. Each sheet of paper is then to be hung up separately, and allowed to dry. These operations may be conducted by candle-light, or in diffused daylight. A stock of this paper may be prepared and kept for use.

2. *Exciting the Paper for the Camera.*—When required for the camera, prepare 1. a solution of *argentic aceto-nitrate* (consisting of 3 grammes of argentic nitrate, 30 cb. centim. of water, and 6 cb. centim. of glacial acetic acid, or 50 grains of argentic nitrate, 1 ounce of water, and 1½ drachm of glacial acetic acid), and 2. an aqueous solution of gallic acid saturated in the cold. Add 3 or 4 drops of each of these solutions to 4 cb. centim. (or 1 drachm) of distilled water, and then in a darkened room apply the mixture freely with a pledget of clean cotton wool to the silvered surface of the iodized paper—when well soaked remove the superfluous portion with a sheet of clean blotting-paper: the same sheet of blotting-paper must not be used twice for this purpose. Whilst still damp it is to be placed between the glasses of the camera slide. It will retain its whiteness for twelve hours or more.

3. *Exposure in the Camera.*—In order to take the photograph of a landscape, a sheet of the prepared paper is exposed in the focus of the camera, and

after the lapse of from five to fifteen or twenty minutes, according to the amount of light, the picture may be withdrawn.

4. *Development.*—The image is developed by brushing the paper over, by means of clean cotton wool, with a mixture of equal parts of the solution of argentic aceto-nitrate and gallic acid. The two solutions must be mixed immediately before they are used, as they speedily undergo mutual decomposition. In a few minutes the picture gradually begins to appear. Any part of the picture which seems wanting in distinctness may be washed over with fresh solution of argentic aceto-nitrate. The development should be effected by candle-light, or in yellow light.

5. *Fixing the Impression.*—As soon as the picture ceases to increase in distinctness, it is to be well washed with water, and immersed in a saturated solution of sodic thiosulphate till the yellow tint of the argentic iodide has disappeared. It is then to be washed thoroughly for several hours in clean water, frequently renewing the water. Unless all traces of the argentic thiosulphate be removed, the picture will gradually lose its intensity. Fox Talbot originally employed a solution of potassic bromide for fixing these pictures, but sodic thiosulphate is to be preferred. When dry, the photograph should be waxed by placing it between two sheets of blotting-paper saturated with white wax, and then passing a moderately heated smoothing iron over the whole. The negative pictures thus obtained may be employed to furnish *positive prints*, or prints with the lights and shadows as they occur in Nature, by Talbot's original 'photogenic' process, or by printing upon a second sheet of the prepared Talbotype paper.*

(127 *h*) *Photography on Collodion.*—An important modification of Talbot's process was introduced by Mr. Archer, who substituted for the iodized paper a transparent film of iodized collodion spread upon glass, as the recipient of the negative picture. The process is thus rendered more certain and very much more rapid, at the same time the manipulation is simplified, whilst the positive pictures obtained by transference of the negative impression are much sharper in their outline. The operation requires to be conducted in a manner different from that which is practised when paper is employed. The following is the method to be pursued:—

1. *To Prepare the Bath of Argentic Nitrate.*—Take of the nitrate 20 grammes, dissolve the salt in 60 cb. centim. of distilled water, and add 1 decigramme of potassic iodide dissolved in 2 cb. centim. of water: then add drop by drop a solution of potassic carbonate till a slight permanent turbidity is produced; afterwards add distilled water until the mixture measures 300 cb. centim.; filter, and add 3 drops of glacial acetic acid.†

2. *Preparation of Solution of Collodion.*—A solution of iodized collodion,

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* For further details upon the subject of photographic printing, &c., the reader is referred to Hardwich's *Manual of Photographic Chemistry*.

† Ordinary argentic nitrate is apt to contain a trace of nitric acid, which it is desirable to neutralize, because an acid solution is much less sensitive to the action of light than a neutral one. It is still more important, however, not to have any alkaline reaction, and as argentic carbonate is slightly soluble in the nitrate, the addition of acetic acid is subsequently made to guard against this: the potassic iodide is added in order to saturate the bath with argentic iodide; if this precaution were not taken, the film of iodized collodion would be liable to lose a portion of argentic iodide, since this salt is also somewhat soluble in a solution of argentic nitrate.

which is suitable for the formation of negative pictures, may be prepared as follows (Hardwich)* :—Take of

Rectified ether (density 0·725) ...	15·	c.c.	or	4 fluid drachms
Alcohol (density 0·805—0·815) ...	15·	c.c.	or	4 fluid drachms
Soluble pyroxylin	0·3	grm.	or	5 grains
Potassic or ammonic iodide	0·13	grm.	or	2 grains
Cadmic iodide	0·13	grm.	or	2 grains

First dissolve the iodides in the alcohol, then add the pyroxylin, and lastly the ether. Agitate the materials well, set them aside for twenty-four hours, and then decant the clear liquid, which will retain sufficient sensitiveness to admit of being used at the end of a month or more after its preparation.

3. *Preparation of the Collodion Film.*—In order to make use of this solution, a plate of glass cut to the size required for the camera (after being washed with a solution of potash to free it from grease, rinsed in water, dried, and wiped, with a clean silk handkerchief), is to be held horizontally in the left hand, and a portion of the collodion is to be poured steadily on the middle of the glass, and by slightly inclining the plate in different directions, made to flow completely over the upper surface: the excess of the solution is immediately to be poured back into the bottle.

4. *Exciting the Plate for the Camera.*—The nitrate bath having been introduced into a trough of glass or of gutta percha sufficiently wide to allow the introduction of the glass plate upon which the collodion is spread—the prepared plate, within half a minute after the film has been poured off its surface, is introduced into the solution of argentic nitrate; in from two to three minutes' time it is thoroughly impregnated with argentic iodide, and when withdrawn from the bath it will exhibit a cream-coloured opalescence. These operations must be effected in a room illuminated by light admitted through a yellow blind, or by the light of a candle screened by yellow glass (127 *v*).

5. *Exposure in the Camera.*—The prepared plate is to be immediately introduced into the slide of the camera, in which it is to be exposed to the object for a few seconds (from 3 or 4 to 30 or 40) according to the nature of the object and the intensity of the light. The slide is then withdrawn from the camera, and the plate, when examined in the darkened chamber, will not be found to exhibit any image.

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* A suitable pyroxylin for this purpose may be obtained in the following manner:—Take of

Oil of vitriol (density 1·843)... ...	180 cb. cm.	or	6	fluid ounces
Water	30 cb. cm.	or	1	fluid ounce
Potassic nitrate (pure)	105 grms.	or	$3\frac{1}{2}$	ounces
Dried cotton wool	4 grms.	or	60	grains

Mix the acid and water, and add gradually the nitre, finely powdered and dried, stirring between each addition, until the whole of the salt is dissolved. Suffer the mixture to cool to 145° or 150° (62° or 65° C.), then add the cotton wool in small tufts at a time, taking care to plunge the cotton completely beneath the surface; cover it, and allow it to stand for ten minutes. Then press out the acid with a glass rod as completely as possible, and throw the pyroxylin into a large volume of cold water, and wash for half an hour; afterwards soak it well in water for 24 hours; lastly, wring it out in a cloth, and dry at a heat not exceeding 100° (38° C.). The substance thus obtained is completely soluble in a mixture of ether and alcohol. It is essential to attend to the strength of the acid and to the temperature employed.

6. *Developing the Image.*—A latent image, however, exists, and it may be developed by the use of a liquid prepared by dissolving—

Pyrogallic acid	0·07 grm.	or	1 grain
Alcohol	0·7 c.c.	or	10 minims
Glacial acetic acid	1·0 c.c.	or	15 minims
Water	30·0 c.c.	or	1 fluid ounce

Half an ounce or more of this liquid is to be poured over the plate immediately after its removal from the camera. The negative image which is thus gradually developed, will be more intense if immediately before using the pyrogallic solution an addition be made to it of the same solution of argentic nitrate as is employed in the bath, in the proportion of 2 drops to each drachm of the developing liquid.

The exact reaction which occurs in this remarkable process is not known. The pyrogallic acid, however, is a substance which has a strong tendency to combine with oxygen; and under the conjoined action of argentic iodide and argentic nitrate (the presence of the latter salt in excess being necessary to the reaction) a portion of silver is reduced probably to the metallic state, and is deposited upon those parts of the film which have been exposed to the action of light.

Other solutions may be employed for developing the latent image. One which answers very well for this purpose consists of—crystallized ferrous sulphate from 12 to 20 grains, glacial acetic acid 20 minims, alcohol 10 minims, and water 1 ounce. It is not, however, so well adapted for the production of intense negatives as the pyrogallic acid. When the picture is sufficiently distinct, it must be washed with clean water, and fixed by immersing it in a solution of sodic thiosulphate (1 part of the salt to 2 of water) till the cream-coloured argentic iodide is entirely removed. A solution of potassic cyanide, containing from 4 to 12 grains of the salt in an ounce of water, may be substituted for the sodic thiosulphate for the purpose of fixing the image. The picture is again to be thoroughly washed in clean water; it is allowed to dry, then heated before a fire until it feels slightly warm, and the film is protected from mechanical injury by covering it with a coat of transparent spirit-varnish by a manipulation similar to that employed in coating the plate with collodion. This varnished photograph may then be employed for procuring positive pictures by means of the sensitive paper prepared with argentic chloride upon Fox Talbot's plan (p. 259). By employing a neutral nitrate bath free from all organic matter, and a collodion which when iodized with potassic iodide remains very nearly colourless, the sensitiveness of the film to the action of light may be so highly exalted, that moving objects, such as the waves of the sea, or a crowd of people, may be successfully depicted by the instantaneous action of light upon the plate.

(127 *i*) *Albuminized Plates.*—Niepce de St. Victor introduced the employment of glasses coated with albumin, prepared by beating up whites of eggs with 1 per cent. of potassic iodide: the liquid is to be placed for 12 or 24 hours in deep vessels, to become clear, after which the supernatant liquid is to be poured upon glass, so as to produce a uniform layer; it is then allowed to dry for 12 hours, and is fit for the bath of argentic nitrate. Albuminized glasses may be preserved for some weeks without injury; they may be excited by means of Talbot's mixture of argentic aceto-nitrate with gallic acid (p. 260). The image is developed by means of a solution of gallic acid after the plate has been exposed in the camera.

(127 *k*) *Photographic Engraving and Lithography.*—In the year 1827, Niepce published a process for obtaining pictures by the aid of light, the basis of which was the fact that the bitumen of Judæa, when exposed to the sun's rays, becomes insoluble in oil of lavender, whilst those parts which have remained

in shadow preserve their solubility. This process has, with some modification, been applied by Niepce de St. Victor, the nephew of the inventor, to the production of engravings upon steel. Powdered asphalt and a proportion of pure bees-wax are dissolved in oil of lavender, and then mixed with an equal volume of benzol. The surface of the steel plate which is to be engraved is first carefully cleaned with whiting and water, after which a solution of hydrochloric acid in 20 parts of water is poured over it, and the plate is immediately washed and dried. The solution of bitumen is then poured upon the plate in a darkened chamber, and dried by the application of a gentle heat. A good *positive* photographic proof is now applied to the surface, covered with glass, and exposed for a short time to the action of diffused light. The exposed plate is next subjected to the action of a mixture of 3 parts of rectified naphtha and 1 of benzol; the parts which have not been exposed to light are gradually acted upon by this mixture. When the process of solution has proceeded far enough, the solvent is washed off with water, and the exposed parts of the plate are 'bitten-in' with a mixture of 1 measure of nitric acid, density 1·33, 2 measures of alcohol, density 0·844, and 8 measures of water. The plate is then submitted to the ordinary processes employed in aqua-tint engraving.

An important modification of a process proposed by Poitevin for producing lithographs by the aid of photography, has been introduced by Mr. Osborne, lately of Melbourne. The basis of this operation is the observation that a mixture of the potassic dichromate (bichromate of potash) and gelatin, when exposed to light, becomes insoluble in water. In order to apply this to practice, 2 parts of gelatin and 1 of the dichromate are dissolved in 8 parts of warm water; when cooled to about 110° (43° C.), 2 parts of albumin from perfectly fresh eggs are added, and the whole is well mixed; the sheets of paper are then coated with this mixture on one side, hung up to dry in the dark, and are glazed by pressure. These operations are conducted in a room illuminated by yellow light. Paper thus prepared may be preserved unaltered for a long time if excluded from light. In order to use it, a negative picture prepared in the usual way is placed over one of these sheets of dichromate paper, and exposed from half a minute to a minute in a good light, with the precautions usual in photographic printing. Owing to the partial reduction of the chromic acid in the parts exposed to light, a positive picture will now be obtained, the parts acted on by light becoming brown, whilst the screened portions retain their original yellow colour. When the picture thus produced is placed in water, the unchanged portions are easily washed away, leaving the altered portions attached to the paper. In practice, it is found best to cover the whole surface of the picture with a coating of lithographic ink, and then float the back of the paper upon boiling water. After soaking for a short time the surface may be sponged, and the screened portion may be completely removed, leaving a beautifully defined positive impression of the negative picture. After washing it with boiling water, the design is, by means of pressure, transferred to the lithographic stone, and the prints, which may be obtained from this transfer in the usual way, are remarkable for their sharpness and delicacy.

Very nearly at the same time as Mr. Osborne, Sir H. James made an independent application of the so-called bichromate process of Asser of Amsterdam to zincography. The liquid which he uses consists of a mixture of 2 measures of a solution of the potassic dichromate (saturated at the boiling point) with 1 measure of a solution of 3 parts of gum arabic in 4 of water, and the transfer is made to a plate of zinc instead of to the lithographic stone. He has applied the process successfully to the copying of old engravings and manuscripts as well as to the multiplication of maps and plans.

(127 *l*) *Autotype.*—This process also depends on the insolubility of a mixture

of gelatin and potassic dichromate after exposure to light. The gelatin is first mixed with colouring matter and spread on paper; after having been sensitized by floating on a solution of potassic dichromate, the film is exposed under a glass negative for a certain time, depending on the intensity of the light. This is measured by an actinometer, consisting of a strip of paper impregnated with argentic chloride, and exposed at the same time until a particular shade is produced.

The gelatin mixture which is in contact with the negative is rendered insoluble over almost the entire surface, since some light penetrates the densest parts of the negative; but this insolubility extends only to a certain depth, the greatest thickness of insoluble matter being of course under the transparent portions of the negative. The soluble portion remains in contact with the paper, and in order to remove this, the film is transferred to a temporary support of porcelain or metal. For this purpose the paper is dipped with the film downwards into water in which the plate is immersed, the metal and paper then removed, and the excess of water squeezed out by means of a wooden rod, from which a piece of thick sheet india-rubber projects. After a few seconds the film adheres firmly to the support, and the whole is placed in hot water; this softens the gelatin so that the paper may be removed and the soluble portions of the film washed away, the insoluble gelatin with the entangled colouring matter remaining on the plate, constituting an inverted picture. A fresh piece of paper is now applied under hot water, and after being squeezed on to the film the whole is allowed to dry, when the film is readily removed from the plate by its adhesion to the paper. The colouring matter employed is usually carbon, so that the prints are permanent.

(127 *m*) *Woodbury-type.*—In this process a thick film of gelatin and potassic dichromate, with a tough layer of collodion on one side, is employed. The side of the film coated with collodion is placed in contact with a glass negative, and printed by direct sunlight. After exposure, the soluble gelatin is removed by washing with water, and the film dried. In this way a picture in relief is produced, which, when dry, is placed on a plate of soft metal, and by means of a hydraulic press the two are squeezed together: on removing the gelatin film a metallic mould is obtained, which is employed for the mechanical reproduction of pictures. A warm solution of gelatin mixed with colouring matter is poured on the mould, and a sheet of resinized paper pressed on to it; after the setting of the gelatin, the paper is removed with the gelatin adhering. When dry the picture is passed through an alum bath, which renders the gelatin insoluble.

(127 *n*) *Heliotype.*—The gelatin film in this process contains, in addition to potassic dichromate, a certain quantity of chrome alum, which renders the gelatin insoluble, but without destroying its power of absorbing water. The film when dry is exposed under a reversed negative, and after printing the back of the film is hardened by the action of light. It is next transferred to a metallic plate, and soaked in water until the unaltered dichromate is removed. The parts of the gelatin which have not been acted on absorb water, which prevents the adhesion of printers' ink which is applied by a roller; the other parts taking the ink freely. Impressions are then taken from the film as in the ordinary process of printing.

(127 *o*) *Chrysotype.*—Other processes more or less analogous to the Talbotype have been contrived: one of them was invented by Herschel, and described by him under the name of the *chrysotype* (*Phil. Trans.* 1842, 206, 209):—Paper is washed over evenly with a solution of ferric ammonio-citrate, of such a strength as when dry to produce a good yellow colour. It is placed in sunshine in a camera, or under any engraving which it may be intended to copy; after a few minutes' exposure, it is to be removed, and instantly washed over with a

neutral solution of auric chloride: a positive picture is thus developed, which assumes great sharpness, becoming gradually deeper up to a certain point; at the instant when it ceases to gain in intensity (this point being easily seized by practice), the picture is put into pure water, and rinsed thoroughly, in order to remove the excess of solution of gold; it is then fixed with a solution of potassic iodide, and again washed to remove the superfluous salts.

In this case the ferric salt, under the influence of the organic matter of the paper, becomes partially reduced to a ferrous salt, in the parts exposed to light; and this ferrous salt, when washed over with the solution of gold, precipitates the gold in the reduced state, and thus gives rise to the coloured image. Water, by removing the excess of the salts, fixes the picture, and prevents it from experiencing further change on exposure to light.

If red prussiate of potash be employed instead of auric chloride, for developing the picture, a blue image will be produced, owing to the formation of Turnbull's blue upon the reduced portions of the salts of iron.

A solution of uranic nitrate may be used instead of ferric ammonio-citrate, and the picture may be developed by means of a solution of argentic nitrate, of auric chloride, or of the salt of some other easily reducible metal.

(127 *p*) *Daguerreotype.*—In the year 1839, Daguerre made known his beautiful method of obtaining photographic pictures upon metallic plates. The essential parts of this process are as follows:—A sensitive film of argentic iodide upon a silver plate is exposed to the action of light in a camera. The latent image is then developed by exposure to the vapour of mercury, after which the picture is fixed by means of sodic thiosulphate.

1. *Polishing the Plate.*—For this purpose a polished sheet of plated copper is taken, and cleaned by rubbing it over first with finely powdered tripoli on a pledget of cotton moistened with a few drops of alcohol, and afterwards with dry cotton, until, when breathed upon, the metal assumes a uniform dull surface, from which the cloud disappears without showing any patches or spots; after this the plate is carefully polished, by means of a long polishing board faced with buckskin. If this preliminary operation be not carefully performed, the subsequent steps will not lead to any satisfactory result; the touch of a finger upon the polished surface is sufficient to soil it.

2. *Iodizing.*—The plate is next exposed for a few minutes to the vapour of iodine, till a thin yellow film is produced uniformly over the surface. This operation should be performed by candle-light, or in a room furnished with a window supplied with yellow glass; the plate must be protected from diffused daylight.

3. *Exposure.*—If such a plate be exposed for a few minutes in the focus of a double achromatic lens, adjusted to a camera obscura in such a manner that the image of the object to be copied shall fall upon the iodized surface, it undergoes an alteration, which, however, is not perceptible on withdrawing the plate from the camera.

4. *Development.*—But if the plate be exposed for a few minutes to the vapour of mercury, heated to about 140° (60° C.), the latent image gradually appears, with all the shadows, lights, and half-tints faithfully reproduced. Much of the success depends upon the proper length of exposure to the action of light, and in this respect practice is the best guide; if too short a time is allowed, the picture is dark and indistinct; if the light has acted too powerfully, the shadows become metallic in appearance, and ill-defined; and if the action be continued for a sufficient length of time, the picture becomes reversed, or *negative*, the shadows in such a case being represented by lights, and the lights by shadows. A due exposure to the mercurial vapours constitutes an important part of the operation; for if this exposure be insufficient, the whites have a bluish cast, and if it be too long continued, the blacks become indistinct and misty.

Mr. Goddard, in the year 1841, discovered that the iodized plate may be rendered very much more sensitive to the action of light, by exposing it for a few seconds to the vapour of bromine, or of chloride of bromine, so as to obtain a mixed film of argentic iodide and bromide, or of argentic iodide, chloride, and bromide. The process was thus rendered applicable to portraits, and the operation could be accomplished in as many seconds as it before required minutes. The usual practice now is, after having obtained an orange-coloured film by exposure of the silver plate to the vapour of iodine, to expose it to the fumes of bromide from bromide of lime, until the film assumes a rose colour; after which it is a second time returned to the iodine box for a period equal to one-third of that occupied by the first iodizing. The plate is then exposed in the camera, after which it is mercurialized.

In order to fix these pictures, Daguerre employed a solution of sodic thiosulphate, and then washed the plates with water. The effect of the Daguerreotype may be much improved by gilding the plate by the process of Fizeau; it is thus rendered less liable to mechanical injury, and a richer and warmer effect is given to the impression:—for this purpose, 1 part of neutral auric chloride and 3 parts of sodic thiosulphate may be dissolved in 500 parts of water: the plate having been placed in a horizontal position, is to be completely covered with a small quantity of this liquid, and the plate is heated by a large spirit-lamp flame until small bubbles appear on its surface. A thin film of reduced gold is thrown down all over the picture, and by this operation the shadows are deepened and the lights rendered more brilliant. Finally, it must be washed with distilled water, drained, and dried by the application of a gentle heat to the back of the plate.

The following theory may be offered in explanation of the changes which occur during the production of the Daguerreotype image:—Under the influence of light, the superficial layer of argentic iodide is modified so as to render it susceptible of decomposition. When the plate is acted upon by the mercurial vapour, the iodine is driven to the deeper layer of silver, and a film of silver is liberated upon the surface of those parts which have been exposed to the action of light, the thickness of this film varying with the intensity and duration of the light. The reduced silver combines with the mercury, and a film of silver amalgam is formed, which varies in thickness with the thickness of the silver film, in consequence of which the reflected tints differ according to the varying thickness of this film: those parts of the iodized plate which have not been exposed to the light, of course do not combine with the mercury. After the plate has been treated with sodic thiosulphate, the excess of argentic iodide is removed, and the blacks consist of metallic silver. Experiment proves that those parts of the plate immediately beneath the highest lights are more deeply corroded than the others, by the action of the iodine which has been driven inwards during the process of mercurialization.

In complete accordance with the foregoing explanation is a curious fact first pointed out by Mr. Shaw, that if a plate after it has received the impression in the camera, but before it has been mercurialized, be exposed to the vapour of iodine or of bromine for a few seconds, the image is completely effaced, and is no longer producible by mercury.

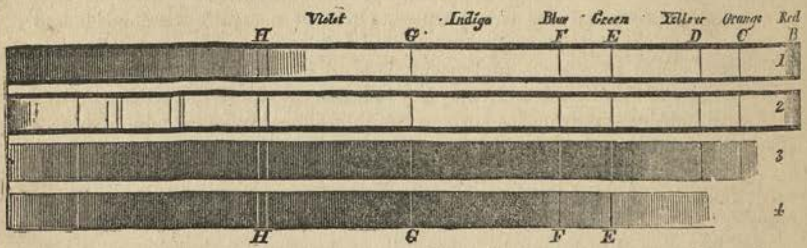
The surface of the plate is rendered uneven by the combined operation of light and mercury upon it, so that it admits of being copied by the process of electrotyping (292). Impressions on paper have been printed from an etched Daguerreotype plate, the biting-in being produced by diluted nitric acid, which attacks the shadows (the reduced silver), and leaves the lights (the amalgam) untouched.

The Daguerreotype process is now almost entirely superseded by photography

on glass, except in cases where extreme sharpness of the image is necessary, as in astronomical photography. The process was employed with success in recording the transit of Venus, Dec. 8, 1874.

(127 *q*) *Photographic Action of the Prismatic Spectrum.*—If a pure solar spectrum, obtained by means of a prism and lens of flint glass, be allowed to fall upon a sheet of sensitive paper, prepared by washing it over first with common salt, and then with argentic nitrate, it will be speedily apparent that the chemical action is not uniformly distributed over the luminous image. The maximum of light falls in the yellow rays about Fraunhofer's line D (fig. 109), whilst the maximum of chemical action occurs

FIG. 109.



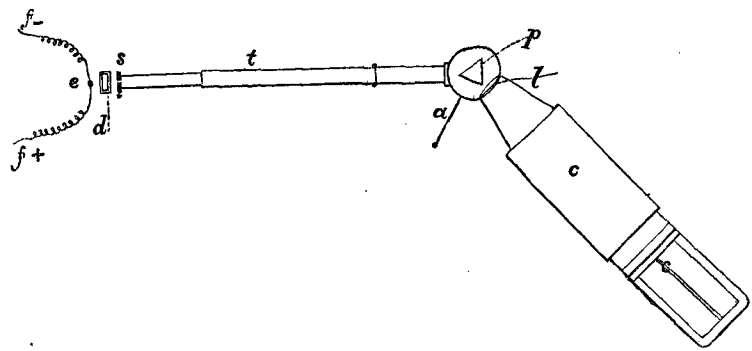
in the blue portion of the spectrum, near the line G, about one-third of the distance between it and the line H. The blackening effect extends nearly as far as F in the green, whilst it is prolonged beyond the violet end of the spectrum to a distance nearly equal to two-thirds of the length of the luminous spectrum, the chemical effect gradually shading off until it becomes imperceptible; the maximum point of action, however, varies with the preparation which is used, and the length of the spectrum varies with the source of light and the material of which the lens and prism are made. When the Talbotype iodized paper is employed, the maximum blackening is found on the extreme limit of the violet rays. Where argentic bromide forms the sensitive material, the chemical action is prolonged towards the red rays, and the greater part of the impression is of a uniform grey black. When paper washed with auric chloride is employed as the sensitive surface, the maximum effect is produced between the green and the blue rays, and the chemical action does not extend beyond the violet extremity for more than half the distance over which these effects are produced upon the salts of silver. In fig. 109, 1 represents the space occupied by the luminous spectrum on white paper; 2, the same spectrum thrown on a fluorescent screen—viz., turmeric paper,—by which it is rendered visible almost to the

extreme limit of chemical action; 3, the chemical spectrum on argentic bromide; 4, the Talbotype spectrum. Herschel, Hunt, and E. Becquerel have each succeeded more or less perfectly in obtaining coloured impressions of the spectrum upon argentic chloride, but they have been unable to fix them. Herschel (*Phil. Trans.* 1840, 19) says that the impression 'was found to be coloured with sombre but unequivocal tints, imitating those of the spectrum itself.' The coloration commenced in the orange rays. E. Becquerel appears to have obtained more brilliant colours by employing a plate of silver which had been superficially converted into subchloride by immersing it in diluted hydrochloric acid, and then making it the positive plate of a voltaic battery.

Inactive spaces occur in the chemical spectrum, which, as Becquerel and Draper have shown, correspond exactly with those which are found in the visible spectrum; but they extend also into the prolongation beyond the violet extremity, and occur there in great number.

These fixed lines may be obtained upon Talbotype paper or, still better, upon a surface of collodion, in the following manner:—

FIG. 110.



Let *c*, *c* (fig. 110), represent a camera which allows of a considerable range of adjustment; *s* is a small slit, admitting of adjustment, but usually presenting a width of about 0·01 inch (0^{mm}·25), through which a beam of solar or other light is either transmitted directly, or is reflected from a heliostat, or from a steel mirror; *l* is a quartz lens with a focal length of from 15 to 30 inches (or from about ·4 to ·75 metre); *p*, a quartz prism, the axis of which is perpendicular to the axis of the crystal, and the refracting faces of which are worked so as to cut the optic axis of the crystal at equal angles. The lens and prism may indeed be made of glass free from striæ, but for accurate observation they must be constructed of rock crystal: the distance of the lens, *l*, from the slit, *s*, is equal to twice its focal length. If the prism be placed so as to produce the minimum deviation of the ray, and as close to the lens as can be, a spectral

image of the aperture will be formed, and may be received upon a screen placed at as great a distance behind the lens, *l*, as *s* is in front of it. All the coarser lines of the visible spectrum may be traced by the unaided eye, when the spectrum is received on a screen of ground glass: and if a sheet of turmeric paper, or a block of yellow uranium glass be used, many of the lines beyond the violet are also rendered visible: by substituting a sensitive surface, such as collodion, for the screen of white paper, a faithful copy of the more refrangible portion of these lines may be obtained.

(127 *r*) It is remarkable that the chemical rays are identical with those which produce fluorescence (110). If the solar rays be transmitted through a layer of a concentrated but colourless acidulated solution of quinine sulphate, or one of æsculin in ammonia, before they reach the photographic surface, but little extra-spectral prolongation of chemical action is produced upon the sensitive surface.

Again, if the solution be removed and the spectrum be received directly upon a screen of yellow uranium glass, or a card coated with a particular uranic phosphate (Stokes, *Phil. Trans.* 1862, 602), a visible prolongation of the chemical rays, crossed by dark lines of inactive spaces, is at once rendered visible.

By varying the source of light, the chemical powers of the spectrum are varied also. The chemical action of the flame of the hydrocarbons, however intense the light, is but feeble; that of the lime-light is much more marked, while that of the electric light between charcoal-points greatly surpasses either; and these results coincide exactly with the relative power of exciting the phenomena of fluorescence possessed by these different lights.

The chemical rays emitted by luminous objects vary greatly both in quantity and in quality, some sources of light emitting rays of much higher refrangibility than others. For example, the flame of ordinary coal-gas burned in admixture with air, so as to produce the blue light of a smokeless gas flame, gives out scarcely any rays capable of affecting an iodized collodion plate; whilst the same amount of gas burned in the ordinary manner for illumination, emits a very decided though limited amount of rays capable of producing chemical action. The rays emanating from the intensely hot jet of the oxyhydrogen flame, are nearly without action upon a sensitive surface of collodion; whilst if thrown upon a ball of lime, though it certainly is not hotter than the burning jet of gas, the light then emitted contains as large a proportion of chemical rays as the solar light, and of very nearly the same refrangibility. But the most remarkable source of the chemical rays is afforded by the light of the electric spark or of the voltaic arc, the chemical spectrum of which is four or five

times as long as the chemical spectrum obtainable from the sun itself.

(127 s) *Photographic Transparency of various Media.*—Amongst the methods of testing the extent of chemical action of any given radiant source, the most convenient is that which is dependent upon the extent of photographic effect exerted upon a surface of collodion coated with argentic iodide, on which the spectrum is allowed to fall.

In no case does it appear that any non-luminous source can emit chemical rays of sufficient intensity to traverse ordinary refracting media; and amongst the rays given off by various luminous objects, it is found that the chemical effects upon the collodion plate are not perceptible in those portions upon which the first three-fourths of the visible spectrum has fallen, but they commence powerfully in the last fourth; and in the case of the electric spark are prolonged to an extent equal to between four and five times the length of the visible portion.

In the prosecution of some inquiries upon the photographic spectra of the metals in which the author was engaged, it was a desideratum to procure some substance which should possess a higher dispersive power than quartz, and which, whilst avoiding the double refraction of quartz, should yet allow the free passage of the chemical rays. He was hence led to try a variety of substances which, owing to their transparency to light, might reasonably be hoped to possess chemical transparency also: for though it was known to those who have studied the spectrum, that many colourless substances besides glass exert an absorptive action upon some of these chemical rays, the subject had not at that time received the careful experimental examination which its importance warrants.

The inquiry soon extended itself beyond the limits originally proposed, and ultimately embraced a large number of bodies in the solid, liquid, and gaseous conditions (*Phil. Trans.* 1862, 861). These experiments showed that although rock-salt, fluor-spar, water, and some few other substances, are almost as *diactinic* (or chemically transparent, from διά, through, ἀκτὶν, a ray) as quartz, none of these bodies could be advantageously substituted for quartz in the construction of the prisms and lenses required in the investigations in which he was engaged.

Among the most remarkable results upon the photographic transparency of bodies are the following:—

1. Colourless solids which are equally transparent to the visible rays, vary greatly in permeability to the chemical rays. 2. Bodies

which are photographically transparent in the solid form, preserve their transparency in the liquid and in the gaseous states. 3. Colourless transparent solids which absorb the photographic rays, preserve their absorptive action with greater or less intensity both in the liquid and in the gaseous states. 4. Pure water is photographically transparent, so that many compounds which cannot be obtained in the solid form sufficiently transparent for such experiments, may be subjected to trial in solution in water.

The mode in which the experiments were conducted was the following:—The source of light employed was the electric spark obtained between two metallic wires, generally of fine silver, shown at *e*, fig. 110, and connected with the terminals of the secondary wires of an induction coil, into the primary circuit of which was introduced a condenser, and into the secondary circuit a small Leyden jar. The light of the sparks was then allowed to fall upon the vertical slit, either before or after traversing a slice or stratum of the material, *d*, of which the photographic transparency was to be tested; the transmitted light was then passed through the quartz prism, placed at the angle of minimum deviation. Immediately behind this was the lens of rock crystal, and behind this at a suitable distance the spectrum was received upon the sensitive surface of collodion. The liquids under trial were contained in a small glass cell with quartz faces, forming a stratum 0·75 inch in thickness, which was traversed by the rays; gases and vapours were introduced into tubes two feet long closed at their extremities with thin plates of polished quartz. The following tables exhibit the relative diactinic power of a few of the various solids, liquids, and gases and vapours subjected to experiment as measured by the *length* of the relative spectra. In some cases the whole length of the spectrum showed evidence of partial absorption of the chemical rays, as the impression was enfeebled throughout its entire length.

PHOTOGRAPHIC TRANSPARENCY OF

Solids.		Liquids, 0·75 in.		Gases and Vapours, 2 ft.	
Rock crystal	74	Water	74	Oxygen	74
Ice	74	Alcohol	63	Nitrogen	74
Fluor-spar	74	Dutch liquid	36	Hydrogen	74
Topaz	65	Chloroform	26	Carbonic anhydride	74
Rock-salt	63	Benzol	21	Olefiant gas	66
Iceland spar	63	Wood-spirit	20	Marsh-gas	63
Magnesic sulphate	62	Fusel oil	20	Hydrochloric acid	55
Borax (solution)	62	Oxalic ether	19	Coal-gas	37
Diamond	62	Glycerin	18	Benzol vapour	35
Potassic bromide (solution)	48	Ether	16	Hydrobromic acid	23
Thin glass (0·009 in.)	20	Acetic acid	16	Hydriodic acid	15
Potassic iodide (solution)	18	Oil of turpentin	8	Sulphurous anhydride	14
Mica (0·007 in.)	18	Disulphide of carbon	6	Sulphuretted hydrogen	14
Potassic nitrate (solution)	16	Arsenious trichloride	5	Air, 0·1 inch pressure	74

The photographic image obtained upon the collodion plate commenced in each case at the same point of the spectrum, corresponding with a spot a little more refrangible than the line G. Calling the line H 100, and numbering backwards for the less refrangible rays, the line B being at 84, the commencement of the photograph in each case is at 96·5, and the extreme limit of the most refrangible rays 170·5.

Each photograph was obtained under circumstances varying only in the nature of the transparent medium through which the rays of the spark from the

silver points were made to pass, before they were allowed to fall upon the collodion plate. When absorption occurs, it is almost always exerted upon the most refrangible rays: but in the case of the coloured gases and vapours, chlorine, bromine, and iodine, the absorption differs from the general rule, and is by no means proportioned to the depth of colour. A column of chlorine with its yellowish-green colour cuts off the rays of the *less* refrangible extremity through fully two-thirds of the spectrum; the red vapour of bromine cuts off about one-sixth to the length of the spectrum, the absorbent action being limited to the less refrangible extremity; whilst the deep violet-coloured vapours of iodine allow the less refrangible rays to pass freely for the first fourth of the spectrum; then a considerable absorption occurs, and afterwards a feeble renewal of the photographic action is exhibited towards the more refrangible end.

In these experiments minute attention to the purity of the substances employed is indispensable: traces of foreign substances inappreciable to ordinary modes of analysis occasionally reveal themselves by their absorptive action on the chemical rays.

Among the various compounds submitted to examination, the fluorides are chemically the most transparent; then follow the chlorides of the metals of the alkalies and alkaline earths; the bromides are less diactinic, and the iodides show a striking diminution in this respect. The group most remarkable for its absorptive power is the nitrates. Nitric acid, whether simply dissolved in water, or combined with bases, has a specific power in arresting the chemical rays; the less refrangible portion it transmits freely, but intercepts the spectrum abruptly at the same point, whatever salt be employed, provided the base be diactinic. The chlorates, it may be remarked, are strongly diactinic.

Glass, even in very thin layers, absorbs the whole of the more refrangible rays.*

Diactinic bases, when united with diactinic acids, usually furnish diactinic salts: but such a result is not uniform: the silicates are none of them as transparent as silica itself in the form of rock crystal. Again, hydrogen is eminently diactinic, and iodine vapour, notwithstanding its deep violet colour, is also largely diactinic; but hydriodic acid gas is greatly inferior to either of them.

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* A hasty consideration of these experiments might lead to the conclusion that lenses of quartz, or of water enclosed in quartz, would be far superior to those of glass in ordinary use by the photographer. This, however, is not the fact. Glass is very transparent to the less refrangible portion of the chemical rays, extending beyond the violet end of the visible spectrum to a distance as much beyond the line H as the red end of the spectrum is below it; and these rays are precisely the most abundant and powerful chemical rays in the solar spectrum, which contains but few rays of a refrangibility much beyond this point, whereas in the electric arc these highly refrangible rays predominate.

The same substance, however, whatever may be its physical form, whether solid, liquid, or gaseous, preserves its character; no chemically opaque solid, though transparent to light, becoming transparent photographically by liquefaction or volatilization; and no transparent solid being rendered chemically opaque by change of form. Hence it is obvious that this opacity or transparency is intimately connected with the atomic or chemical character of the body, and not merely with its state of aggregation. Although the absorption of the chemical rays varies greatly in the different gases, which therefore in their action display an analogy to their effects upon radiant heat, yet those gases which absorb the rays of heat most powerfully are often highly transparent to the chemical rays, as is seen in the case of aqueous vapour, of carbonic anhydride, cyanogen, and olefiant gas, all of which are compound substances, not chemical elements. Compounds as *compounds* do not appear to act more energetically as absorbents than simple bodies.

The abrupt termination of the chemical spectrum in coal-gas is remarkable: in that case the absorption appears to be due, not to the permanent gases, but to the vapours of benzol, and other heavy hydrocarbons that it contains.

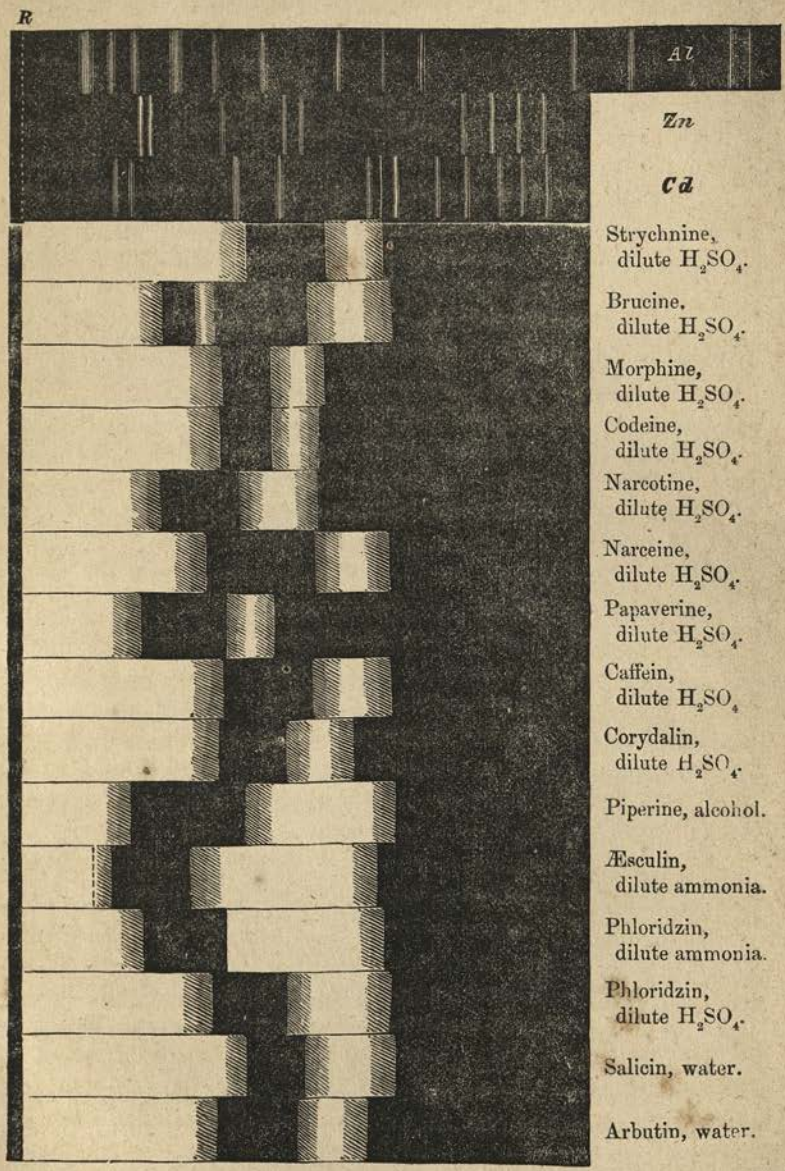
In the case of reflection from polished surfaces, the metals were found to vary in the quality of the rays reflected; gold and lead, although not the most brilliant, reflecting the chemical rays more uniformly than the brilliant white surface of silver and speculum metal.

Stokes (*Phil. Trans.* 1862, 606) has pursued this investigation in a different manner; instead of photographing the spectra, he submitted them to ocular inspection, by receiving the invisible rays upon a fluorescent screen.

He found that the vegetable alkaloids and the glucosides are, almost without exception, intensely opaque for a portion of the invisible rays absorbing them with an energy comparable, for the most part, to that with which colouring matters, such as indigo or madder, absorb the visible rays. The mode of absorption is also generally highly characteristic of each compound, and frequently very different in the same body, according as it is examined in an acid or an alkaline solution. In the examination, a small cell, with parallel faces of quartz, or sometimes a wedge-shaped vessel, with its inclined faces also of quartz, was employed. The cell being filled with the solvent, water, dilute acid, dilute ammonia, or alcohol, &c., a minute quantity of the substance under trial is introduced, and the absorptive effects exerted are watched

as the substance gradually undergoes solution. Fig. 111, below, is taken from Stokes's paper. The bold lines of alu-

Fig. 111.



minium, zinc, and cadmium, are given as points of reference; the border on the left is the limit of the red light visible on the

screen. The dotted line in the figure for æsculin denotes the commencement of the fluorescence, which is situated near the line G of the solar spectrum, the luminous portion of which does not extend beyond the termination of the first portion of the spectrum of piperine. Stokes remarks that in the figure the shading merely represents the general effect, the gradation of illumination not having been registered; and although the central parts of the maxima of transparency are left white, in reality there is almost always some absorption. The effect of acids and alkalies on the glucosides presents one uniform feature: when a previously neutral solution is rendered alkaline, the absorption begins somewhat earlier, when rendered acid somewhat later, than in a neutral solution.

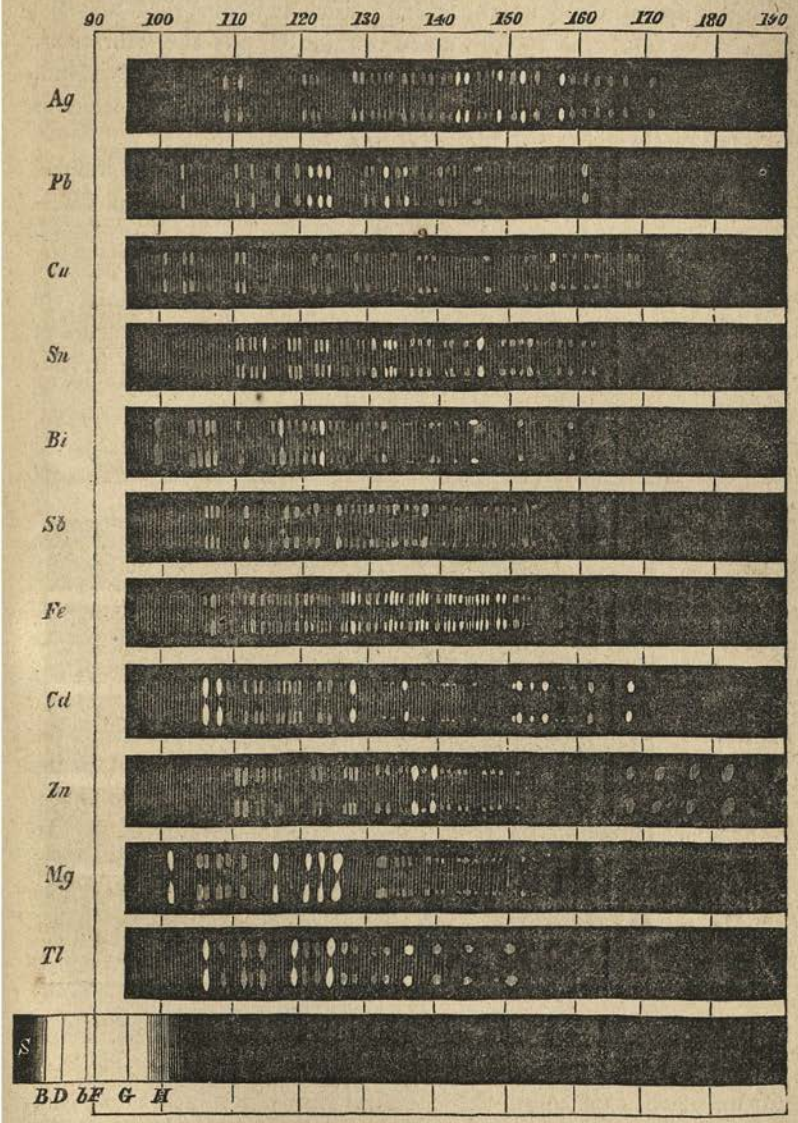
(127 *t*) *Photographic Spectra of the Elements.*—Equally interesting are the results obtained by examining the spectra produced by varying the nature of the metallic electrodes employed as terminals to the secondary wires of the induction-coil. Wheatstone showed many years ago that the visible spectrum of each metal is perfectly characteristic when electro-magnetic sparks are transmitted between two surfaces of the metal; and I have found that the same thing is equally true of the invisible portion of the spectrum.

Even the various gaseous media become so intensely heated by the passage of the electric spark, that they furnish photographic spectra, each of which is characteristic of the body which occasions it, and when the electric discharge of the secondary coil becomes intensified by use of the Leyden jar, the sparks not only produce the spectra due to the metals, but to the gaseous medium in which the electrodes are immersed; so that a mixed spectrum is the result. The spectra produced by the metals are characterized by bands of which the extremities only are visible; whilst the gaseous spectra yield continuous lines which traverse the whole width of the spectrum. When a compound gas is made the medium of the electric discharge, the spectra produced are those of the elementary components of the gas. It seems as though at these intense temperatures chemical combinations were impossible; and at temperatures as intense as those obtained in the voltaic arc, oxygen and hydrogen, chlorine and the metals probably all coexist in a separate form, though mechanically intermingled.

The spectrum produced by the ignition of a solid or a liquid always yields a continuous band of light, containing rays of all degrees of refrangibility; but the same body, when converted

into vapour, produces a spectrum consisting of a series of bright bands of particular colours, separated from each other by in-

FIG. 112.



tervals more or less completely dark, incandescent gaseous bodies emitting rays of certain definite refrangibilities only (109).

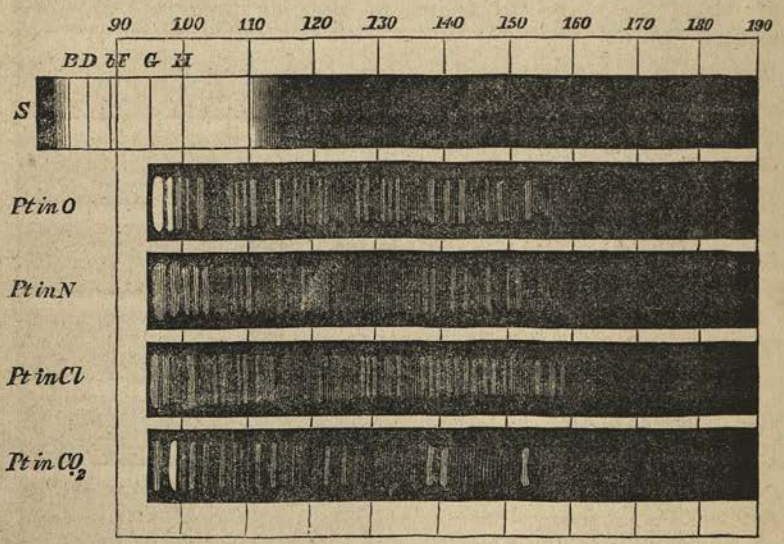
From the striped character of the photographic spectra, it is obvious that the vibrations are emitted from the different metals

in the form of vapour, and not merely in that of detached particles projected from the electrodes by disruptive discharge.

This observation may give some idea of the intensely high temperature attained by the spark; since it is observed that the higher the temperature, the more refrangible are the vibrations. We are, indeed, furnished in this case with a rude, but still, under the circumstances, with a valuable pyrometric means of estimating these exalted temperatures.

Fig. 112 exhibits a few of the spectra of the metals obtained by the secondary spark, contrasted with the solar spectrum transmitted through the same lens and prism under similar circumstances: the spectra of oxygen, nitrogen, chlorine, and carbonic anhydride, produced by sparks between platinum points, are also given in fig. 113. Platinum has but a feeble spectrum of its own; and it does not appear in the spectra given in this figure.

FIG. 113.



(127 *u*) *Extinction of Chemical Rays.*—Bunsen and Roscoe (*Phil. Trans.* 1857, 601) have made experiments on the absorbent power of chlorine upon the chemical rays which affect the combination of a mixture of chlorine and hydrogen. They find that when light passes through a medium in which it excites chemical action, a quantity of light is absorbed proportional to the chemical effect produced. For instance, the chemical power of the light of a coal-gas flame of a certain intensity, measured by its activity in

producing the combination of chlorine with hydrogen, was found to be reduced to one-tenth when transmitted through a column of chlorine 6·811 inches ($173^{mm.}$) in depth; if the chlorine were diluted with an equal volume of air, the length of the column required to produce a similar absorption was exactly double, or 13·622 inches ($346^{mm.}$). But when a mixture of equal volumes of chlorine and hydrogen was used, the depth of the mixture which was required to reduce the chemical effect of the light to one-tenth of its original intensity was only 9·212 inches ($234^{mm.}$); hence it appears that a certain quantity of the active rays are absorbed during the production of a given chemical effect.

With light from different sources, analogous results were obtained, but the amount absorbed was found to vary with the source of the light. For instance, the diffused zenith light of a cloudless sky in the morning was reduced to one-tenth of its intensity by transmission through 1·795 inch ($45·6^{mm.}$ of chlorine, and through 2·894 inches ($73·5^{mm.}$) of a mixture of chlorine and hydrogen; the absorbent action of chlorine upon the chemical rays of diffused daylight being much more energetic than on those emitted by burning coal-gas. Observations made with evening light showed that a depth of 0·776 inch ($19·7^{mm.}$) of chlorine was sufficient to reduce the chemical power to one-tenth of that possessed by the incident light. The relative thickness of the stratum of chlorine required to produce an equal reduction in the chemical power of the incident light was therefore the following:—

	Inches.	Millimetres.
A flame of coal gas	6·811	173
Reflected zenith light (morning) . .	1·795	45·6
Reflected zenith light (evening) . . .	0·776	19·7

(127 *v*) It was stated more than 60 years ago by Ritter, and the observation was confirmed and extended by Sir J. Herschel, that the two ends of the spectrum produce opposite chemical effects, though the violet extremity appears greatly to predominate in power. If, for example, paper soaked in argentic nitrate be partially blackened by exposure to diffused daylight, and then submitted to the action of the solar spectrum, the portion upon which the violet end falls speedily becomes much darker, while the portion beneath the red rays assumes a brick-red hue. If the spectrum be thrown upon white paper coated with argentic nitrate, and diffused daylight be allowed at the same time to fall upon it, the spot where the red rays fall retains its whiteness, while the rest of the paper speedily darkens. It thus appears, that by combining the influence of two rays of different refran-

gibilities, effects are producible which cannot be obtained by either ray separately.

Paper soaked with argentic nitrate and blackened by the action of light, if washed over with a solution of potassic iodide, becomes gradually bleached when exposed to diffused daylight. If the solar spectrum be allowed to fall upon paper thus prepared, whilst moist, and before it has become bleached, the part beneath the violet end is quickly bleached; but this effect is bounded by a sharp border in the yellow, while the paper under the red end becomes darker. The phenomena of phosphorescence also exhibit similar opposition in the effects produced by the opposed extremities of the spectrum (112).

Claudet (*Phil. Trans.* 1847, 256) found that an iodized Daguerreotype plate, when submitted in the focus of a camera to the red image of the sun as seen through a London fog, became subsequently whitened on exposure to the vapour of mercury, in all parts except in the track traversed by the image of the sun—this portion continued to be perfectly black. In another experiment, a plate was covered with black lace, and exposed to diffused daylight: after a few minutes' exposure, the lace was removed, one-half of the plate was then covered with an opaque screen, the other half with a red glass, and the exposure was continued for a short time: in the mercury box the red half continued to be black, whilst on the other portion the image of the lace was distinctly traced. The photographic effect at first produced over the whole plate had in fact been neutralized by the red glass.* A pleasing variation of the last experiment was made by exposing an iodized plate to diffused daylight, then covering it with a piece of black lace, and screening it with a red glass; a negative picture was now developed in the mercury box, the red glass having destroyed all photographic action except on those parts screened by the lace. Orange and yellow glasses give similar results. After exposing a plate to daylight, and then submitting it to the action of light passing through red glass, it again becomes sensitive to light, so that, as Claudet observes, it is no longer needful to prepare the plates in a dark chamber, since, if placed beneath a covering of red glass, they are always ready for immediate use—even though subsequently to their preparation they may have been for some time exposed to solar light.

But though the red and yellow glass have the power of completely counteracting the effect of the radiation of the more refrangible rays, they have a peculiar effect of their own. The neutralizing power of the red ray is exerted more slowly than the photographic effect of the white light, nearly in the proportion of 100 to 1; that of the yellow ray was found to be about that of 10 to 1.

From the foregoing remarks, it is evident that the colour of objects must exert a material influence upon the nature of the photographic image produced. Reds and yellows, from the want of chemical energy in the less refrangible portion of the spectrum, will be characterized by absence of photographic action in the image, and will be represented by black spots, which often produce singular disfigurement in portraits. Yellow freckles, for instance, on the skin of the face are accurately copied, but are depicted in the portraits as black spots. Much judgment and knowledge are therefore required in selecting a dress of a colour which is adapted to produce a suitable depth and contrast of tint in the photograph.

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* It must be borne in mind that all results obtained by coloured media are liable to ambiguity, for it seldom happens that the light transmitted through them is homogeneous (105); the effects are liable to become complicated from the intermixture of results produced by rays from different parts of the spectrum.

(127 *w*) *Action of the Solar Spectrum on Vegetable Colours.*—This subject has been particularly examined by Herschel (*Phil. Trans.* 1842, 188). White paper coloured with various vegetable juices was subjected by him to the influence of the prismatic spectrum, and in some cases these papers were washed over with solutions of metallic salts. The following are the most important general conclusions which may be drawn from these experiments:—1. That the action of light is in almost all cases of a nature to obliterate the colour; or if it does not entirely bleach it, a faint residual tint is left, upon which it has little further action. The older the paper or the tincture, the more decided is this residual tint, which is probably the result of an oxidizing action upon the colouring material, independent of the action of light. 2. The action is confined to *luminous* rays of the spectrum—offering in this respect a marked difference between these actions and those produced upon the metallic compounds. 3. The rays which are most effective in destroying a given tint are in many cases those which are complementary (105) to the tint destroyed. Orange-yellows, for instance, are bleached most powerfully by the blue rays: blues by the red, orange, and yellow rays; and purples and pinks by the yellow and green rays.

CHAPTER V.

HEAT.

§ I. *Expansion.—Measurement of Temperature.*—§ II. *Means of maintaining Equilibrium of Temperature.*—§ III. *Specific Heat, Latent Heat.*—§ IV. *Heat of Combination.*

(128) *General Effects of Heat.*—Upon the due understanding of the principles and applications of heat, much of the successful prosecution of chemical research depends. There is scarcely a chemical operation in which heat is not either emitted, absorbed, or purposely applied to produce the required result. Heat in one mode of its manifestation presents the closest analogy with light, which it very generally accompanies. In this condition it is known as radiant heat: and it is in this form that the supply of heat is transmitted from the sun to the surface of the earth.

It is, however, after heat has fallen upon the surface of an object and has become absorbed, that its most important effects are manifested. It is only then that the sensation of warmth is

experienced; then it is that expansion takes place in the heated body; and it is then only that the phenomena of liquefaction or of evaporation may ensue. Heat may also, after its absorption, be again transmitted from the heated body, by secondary radiation, to other objects around, or it can be propagated more slowly by conduction from particle to particle through the mass.

Other most important effects of heat are seen in the change of state in bodies from the solid to the liquid and from the liquid to the gaseous condition. Whenever a solid becomes liquid, or a liquid becomes converted into vapour, the change is attended with the disappearance of a quantity of heat, which is perfectly definite; for instance, a pound of ice in undergoing liquefaction always requires the same quantity of heat to produce this effect; the water obtained appears to be no warmer than the ice; but the heat, though it for a time ceases to affect the senses, is not lost, for it reappears when the water passes back into the state of ice. The heat which disappears in liquefaction is said to have become latent; and it again becomes sensible as the solid condition is resumed. Finally, it is found that the quantity of heat produced by the chemical actions of definite amounts of matter upon each other is definite, whether the chemical action occur rapidly or slowly.

In considering the relations of heat, the subject may therefore naturally be subdivided into four sections:—

The first of these embraces the phenomena of *expansion*, and their application to the measurement of temperature, including the principle of the thermometer and the pyrometer: the second refers to the modes in which the *equilibrium of temperature* is sustained or restored—viz., by conduction, by convection, and by radiation as well as the phenomena of specific heat: the third relates to the latent *heat of liquefaction and vaporization*, including the processes of congelation and liquefaction, and those of ebullition and evaporation: whilst the fourth embraces *heat of combination*, or the quantitative estimation of the heat evolved by chemical action.

Before passing to the immediate consideration of these subjects, it will be advantageous to review briefly the principal means at our command for procuring a supply of heat by artificial means.

(129) *Sources of Heat.*—1. The sun obviously affords the main supply of warmth to the globe. It may furnish some aid towards a conception of the enormous amount of heat continually emanating from the sun, when we state that, calculating from the

mean distance of the earth from the sun, and from the area which the earth exposes to the solar rays, the quantity of heat which reaches the earth is not at any given moment more than the two thousand three hundred and eighty millionth part of that emanating from the sun.

2. There are, however, many other sources whence heat may be procured. *Friction* is one of them. Some savage nations employ the friction of two pieces of dry wood as a means of obtaining fire; and it is known among ourselves that the axles of wheels and other parts of machinery sliding in contact sometimes become so much heated as to char or ignite the woodwork in their immediate vicinity.

In order to obtain some idea of the amount of heat produced by friction, the following experiments were instituted by Count Rumford (*Phil. Trans.* 1798, 80): —A brass cannon, weighing 113 lb., was made to revolve horizontally with a pressure of about 10,000 lb. against a blunt steel borer, at the rate of 32 revolutions per minute; in half an hour the temperature of the metal had risen from 15° C. to 55°; this heat would have been sufficient to have raised 5 lb. of water from 0° to 100° C. The experiment was subsequently varied by placing the cannon in a vessel of water, and friction was again applied; in this case, 18¾ lb. of water at 15° C. were actually made to boil in two hours and a half. The heat thus obtained was calculated by Count Rumford to be somewhat greater than that given out during the same period by the burning of nine wax candles each ¾ inch in diameter.

One of the most remarkable proofs of the generation of heat by friction was afforded in an experiment by Davy, in which two pieces of ice, made to rub against each other *in vacuo*, at a temperature below 0° C., were melted by the heat developed at the surfaces of contact.

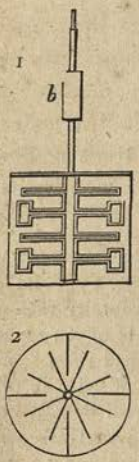
The experiments of Joule (*Phil. Trans.* 1850, 61) appear to show that the actual quantity of heat developed by friction is dependent simply upon the amount of work expended, without regard to the nature of the substances rubbed together. He found, as a mean of forty closely concordant experiments, that when water was agitated by means of a horizontal brass paddle-wheel, made to revolve by the descent of a known weight, the temperature of 1 lb. of water was raised 1° F. by the expenditure of an amount of work sufficient to raise 772·7 lb. 1 foot high. When cast-iron was rubbed against iron, the work required to raise 1 lb. of water 1° F. was found, as a mean of twenty experiments, to be about 775 foot pounds; and by the agitation of mercury by means of an iron paddle-wheel it was found to be 774 foot pounds.

The conclusion drawn from these experiments was—that the quantity of heat capable of raising the temperature of 1 lb. of

water (between 55° and 60°) by 1° F. requires for its evolution the expenditure of work adequate to lift 772 lb. 1 foot. This may be expressed in terms of the metrical system as follows:—

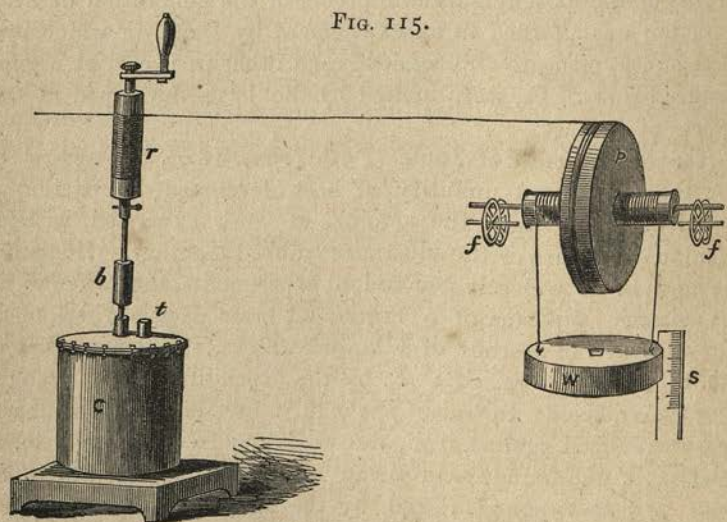
A *unit of heat*, or the heat capable of raising 1 gramme of water 1° C., is equivalent to work required to lift 423·55 grammes through a height of 1 metre.

Fig. 114.



The apparatus employed in the determination of the amount of heat given out during the friction of water consisted of a brass paddle-wheel furnished with eight sets of vanes, revolving between four sets of stationary vanes. Fig. 114, No. 1, shows a vertical section of the paddle, and No. 2 a transverse section of the vessel and paddle. This paddle was fitted securely into a copper vessel, C, fig. 115, provided with a lid in which were two apertures, one allowing the passage of the axis without actual contact with it, the other *t*, for the insertion of the thermometer graduated to hundredths of a degree F. A weighed quantity of water was introduced into the vessel, or *calorimeter*, C, and its temperature ascertained with minute precision. The amount of heat produced was ascertained by again observing the temperature of the water in C, with the same precision, at the close of each experiment. In order to prevent loss of heat by conduction, the vessel was supported upon a wooden stool, and connected by a piece of boxwood, *b*, with the apparatus for producing rotation. Motion was given to the axis by the descent of two leaden weights, one of which is shown at W, fig. 115. These weights were suspended by strings over two

Fig. 115.



wooden pulleys, one of which is shown at *p*, resting on friction rollers, *f. f*, and the pulleys were connected by fine twine with the roller *r*, which, by means of a pin, could be readily connected with, or detached from the calorimeter, C. The descent of the weights was measured on the scale, S.

A similar, but smaller apparatus, made of iron instead of brass, with six rotatory and eight stationary vanes, was used for measuring the heat produced by the friction of mercury. The apparatus for measuring the heat produced by the friction of solids, consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a stationary bevelled wheel was pressed by a lever; the wheels were enclosed in a cast-iron vessel filled with mercury.

The rise of temperature in each experiment amounted in the case of water to about 0°·313 C., or 0°·563 F. In the case of mercury, the mean rise during each experiment in one series was 1°·339 C., or 2°·41 F., and in case of cast-iron, it was 2°·39 C., or 4°·3 F.

3. *Percussion*, which is a combination of friction and compression, is a method of eliciting heat which is frequently practised, as is seen in the use of the common steel and flint, where the compression developes heat enough to set fire to the detached portions of steel. In firing iron shot against an iron target, as in the artillery trials at Shoeburyness, a sheet of flame is commonly seen at the moment of the collision, owing to the arrest of motion in the projectile, and its manifestation in the form of heat. Mr. Whitworth has indeed employed iron shells which are exploded simply by the heat developed by the concussion on striking the surface of the iron target. It is a practice not uncommon among blacksmiths, to show their agility and dexterity by hammering a piece of cold iron on the anvil until it becomes red-hot from the heat produced by compression. It is, however, remarkable that iron once treated in this way cannot again be made red-hot by hammering unless it has been subsequently heated in the forge. Many other similar instances might be adduced; in the rolling of brass and of copper, for example, the bars, as they issue from the rollers, between which they have been subjected to enormous pressure, become much heated, although they were quite cold when they entered the rolling mill.

4. Another source usually resorted to for procuring heat artificially is *chemical action*. Whenever this occurs with great intensity, heat is evolved, and it is very generally accompanied by evolution of light, of which a common fire affords the best practical illustration. The chemical actions which are constantly going on in living animals are also never-ceasing sources of a regulated emission of heat, and they differ only from those of the furnace in the more moderate and subdued amount of heat generated in a given time and in a given space. The quantity of heat generated by the combination of definite weights of the bodies which unite is perfectly definite in amount, depending only on the quantity and quality of the substances entering into combination. (199 *et seq.*)

5. Accumulated *electricity* is another source of intense heat.

6. In addition to the above-mentioned sources of heat, Pouillet (*Ann. Chim. Phys.* 1822 [2], xx. 141) has shown that the simple act of *moistening* any dry substance is attended with slight yet uniform disengagement of heat. With bodies of mineral origin, when reduced to a fine powder with a view of increasing the extent of surface, the rise of temperature does not exceed from 0°·3 to 1° C.; but with some vegetable and animal substances, such as cotton, thread, hair, wool, ivory, and well-dried paper, a rise of temperature varying from 1° to even 6° C. has been observed.

7. Besides these sources of heat there can be no doubt of the existence of a nucleus of intensely heated matter within the body of the earth itself. If a thermometer be buried from 10 to 12 metres beneath the surface, it is found to undergo no change with the alternations of the seasons, but on proceeding to greater depths the thermometer is found to rise progressively, though not quite uniformly at all places. If it be assumed that on the average this increase of temperature is 1° C. for every 29·3 metres of descent,* and if this rate of progression be continued uniformly as the depth increases, it would be at the rate of 55° C. or 100° F. per mile; so that at a depth of a mile and a half the temperature would be as high as that of boiling water, and at the depth of 40 miles, a temperature of 2204° C. (4000° F.) would be attained, considerably beyond the melting point of cast-iron or even of platinum. The existence of this central heat, which rises to a degree sufficiently high to fuse the rocky constituents of the earth's crust, is abundantly manifested in the torrents of melted lava which are from time to time poured forth in volcanic eruptions; and the occurrence, at great depths, of rocks which bear evident marks of igneous action, attests the high temperature of the interior of the earth.

(130) *Nature of Heat—Mechanical Theory of Heat.*—Two principal views of the nature of heat have been entertained since experimental science has been actively cultivated. One of those views, which is supported chiefly by the phenomena of latent heat and chemical combination, regards heat as an extremely subtle material agent, the particles of which are endowed with high self-repulsion, are attracted by matter, but are not influenced by

* Cordier considers 1° C. in 25 metres, or 1° F. in 45 feet, not too high an estimate. In two shafts of the depth of 2000 feet, one near Durham and the other near Manchester, the temperature increases 1° F. for 65 to 70 feet; in the Saxon argentiferous lead mines, it was found to be 1° in 65 feet, and the increase of temperature observed in boring the well of Grenelle at Paris was 1° in 60 feet.—Lyell, *Princ. Geol.* 11th ed. ii. 205.

gravity. On the other theory heat is supposed to be the result of molecular motions or vibrations.

The latter view was powerfully advocated by Count Rumford, and by Davy, who, in the early part of the present century, instituted an important series of experiments upon the production of heat by friction. Many philosophers were subsequently induced to adopt the theory of the vibratory nature of heat as maintained by these eminent men. The opinions of Davy upon this subject are thus stated by him in his treatise on *Chemical Philosophy*, p. 95. 'It seems possible to account for all the phenomena of heat, if it be supposed that in solids the particles are in a constant state of vibratory motion, the particles of the hottest bodies moving with the greatest velocity, and through the greatest space; that in liquids and elastic fluids, besides the vibratory motion, which must be conceived greatest in the last, the particles have a motion round their own axes, with different velocities, the particles of elastic fluids moving with the greatest quickness; and that in etherial substances the particles move round their own axes, and separate from each other, penetrating in right lines through space. Temperature may be conceived to depend upon the velocities of the vibrations; increase of capacity, on the motion being performed in greater space; and the diminution of temperature during the conversion of solids into fluids or gases, may be explained on the idea of the loss of vibratory motion, in consequence of the revolution of particles round their axes, at the moment when the body becomes fluid or æriform, or from the loss of rapidity of vibration in consequence of the motion of the particles through greater space.'

The experiments of Joule on the definite amount of heat developed by friction (*Phil. Trans.* 1850, 61) have recalled the attention of philosophers to these views; and the mathematical theory of heat propounded by S. Carnot, in accordance with them, has undergone recent revision, particularly by Mayer, Clausius, Rankine, and Sir W. Thomson, in consequence of which the hypothesis involved in the term *the mechanical theory of heat* has been favourably received. Upon this view, although the ideas of Davy quoted above have been adopted with extensions and modifications by some writers, it is not necessary to assume the particular kind of motion in the interior of bodies which may be conceived to be the cause of the peculiar phenomena of heat, but only to suppose that a motion of the particles exists, and that the heat is a measure of the kinetic energy of this motion. The important principle of the theory is this:—*In all cases where mechanical work is produced by heat, a quantity of heat is used up, proportional to*

the work done: and, conversely, the same quantity of heat can be again generated by the expenditure of just so much mechanical effect.

Tyndall, in his work on *Heat considered as a Mode of Motion*, has applied the mechanical theory of heat to the explanation of many of its phenomena with great ingenuity and clearness. The chemical considerations, which are indeed the most difficult to reconcile with this theory, are, however, only incidentally touched upon by him. A simple view of the mathematical considerations involved is given in B. Stewart's *Elementary Treatise on Heat*, and Maxwell's *Theory of Heat*.

§ I. Expansion—measurement of temperature.

(131) *Difference between Heat and Temperature.*—The effect of a hot or of a cold substance upon our sensations enables us to distinguish the one from the other; but the impression thus produced is only comparative, and affords no exact criterion of the amount of heat, the sensation produced being referable to the temperature of that part of the body to which the substance is applied at the particular moment. Heat and cold are, in fact, merely relative terms; cold implying not a negative quality antagonistic to heat, but simply the absence of heat in a greater or less degree. It is singular that intense cold produces the same sensation as intense heat; and a freezing mixture, as well as boiling water, will blister the part to which it is applied.

Heat produces no alteration in the weights of bodies; consequently the balance cannot be employed as a measure of its amount. All bodies, however, when heated, acquire an increase in volume, and return to their original volume in cooling, and the measure of the amount of expansion is universally employed as the measure of temperature.

It is necessary to draw a distinction between the terms *heat* and *temperature*, which are applied to indicate very different things. By the term heat is meant, in philosophical language, the power, whatever it be, which excites in us the sensation of warmth; temperature is a measure of the tendency of a body to impart heat to other bodies: bodies are at equal temperatures when neither transfers heat to the other. If two or more masses of matter, of the same or of different kinds, such as mercury, oil, water, or spirit of wine, when brought into contact with a thermometer, cause the mercury which this instrument contains to stand at the same point, they are said to have the same temperature. But the temperature of a body affords no indication of

the actual quantity of heat which it contains. A pint of spring water may raise a thermometer to the same degree as a gallon of the same water, though it is obvious that the larger quantity of the liquid contains the greater amount of heat. Again, suppose a thermometer to stand in water at 40° in one instance, and at 80° in another, in equal quantities of the liquid; it would be a mistake to suppose that in the latter case the water is twice as hot as in the former. The zero of the thermometer scale is an arbitrary point; the temperature of a body which contained no heat or the zero of a perfect thermometer scale would be −273° C. or −459°·4 F.

(132) *Expansion of Solids.*—Solids, as might be expected from the cohesion among the particles, expand less for equal elevations of temperature than either liquids or gases. Solids generally expand uniformly in all directions, and on cooling return to their original shape. Lead, however, is so soft that its particles slide over each over in the act of expansion, and do not return to their original position. A leaden pipe of a few feet long, if used for conveying steam, becomes permanently lengthened by some inches in a short time; and the leaden flooring of a sink which often receives hot water, becomes, in the course of use, thrown up into ridges and puckers.

Mitscherlich (*Poggendorff's Ann.* 1827, x. 137) discovered that all those crystals which possess a doubly refracting action upon light, expand unequally in different directions when heated. The shape of a crystal of calcareous spar, for instance, is slightly altered when heated: the obtuse angles become more acute, and the inclination of the faces of the crystal to each other becomes lessened 8½′ by an elevation of temperature from 0° to 100° C. The crystal elongates most in the direction of the optic axis, and indeed it actually contracts at the same time in directions at right angles to this. Such crystals, however, form no exception to the general rule that the volume of bodies is increased by heat. It has been ascertained, for instance, that a crystal of calc-spar increases in volume between 0° and 100° C., to the extent of 1 part in 510.

Different solids expand very unequally for equal increase of temperature: zinc, for example, expands much more than iron, and iron more than glass. The cubical expansion of a body may be obtained very nearly by multiplying the linear expansion (or expansion in length) by 3. The following table gives some measurements of the expansion both in length and in volume which is experienced by various solid bodies:—

Expansion of Solids.

1 Part at 0° C. or 32° F.	At 100° C. or 212° F. become,	Expansion, In Length.	Expansion, In Volume.	Authority.
English Flint Glass	1·000,811	1 in 1233	1 in 411	Lav. & Laplace
Glass tube (French)	1·000,871	1 in 1148	1 in 382	Dulong and Petit
Platinum	1·000.884	1 in 1131	1 in 377	Dulong and Petit
Palladium	1·001,000	1 in 1000	1 in 333	Wollaston
Untempered Steel	1·001,079	1 in 926	1 in 309	Lav. & Laplace
Antimony	1·001,083	1 in 923	1 in 307	Smeaton
Iron	1·001,182	1 in 846	1 in 282	Dulong & Petit
Bismuth	1·001,392	1 in 718	1 in 239	Smeaton
Gold	1·001,466	1 in 682	1 in 227	Lav. & Laplace
Copper	1·001,718	1 in 582	1 in 194	Dulong & Petit
Brass	1·001,866	1 in 536	1 in 179	Lavoisier and Laplace
Silver	1·001,909	1 in 524	1 in 175	Lavoisier and Laplace
Tin (East India)	1·001,937	1 in 516	1 in 172	Lavoisier and Laplace
Lead	1·002,848	1 in 351	1 in 117	Lavoisier and Laplace
Zinc	1·002,942	1 in 340	1 in 113	Smeaton

The following results, which were obtained by Daniell, with bars heated in a cylinder of baked black-lead ware, and measured by his pyrometer scale (140), show the expansion of certain solids at high temperatures. (*Phil Trans.* 1841, 456.)

Linear Expansion of Solids.

1,000,000 Parts at 16° C. or 62° F.	At 100° C. or 212° F.	At 350° C. or 662° F.	At Fusing Point.
Black-lead Ware	1000244	1000703	
Wedgwood Ware	1000735	1002995	
Platinum	1000735	1002995	1009926 maximum, but not fused.
Iron (Wrought)	1000984	1004483	1018378 to the fusing point of cast-iron.
Iron (Cast)	1000893	1003943	1016389
Gold	1001025	1004238	
Copper	1001430	1006347	1024376
Silver	1001626	1006886	1020640
Zinc	1002480	1008527	1012621
Lead	1002323		1009072
Tin	1001472		1003798

The addition of heat beyond a certain point overcomes the cohesion of the solid, and it assumes the liquid form. The temperature at which this change takes place varies greatly with the nature of the substance, some solids melting at a much lower temperature than others.

(133) *Expansion of Liquids.*—Liquids expand much more than solids. They differ also in expansibility to a much greater

extent: generally the most volatile are most expansible. This is remarkably shown in the case of the liquids obtained by the condensation of the gases (196), which are even more dilated by heat than aëriform bodies.

Expansion of Liquids.

At 0° C. or 32° F.			At 100° C. or 212° F.	Expansion.	Authority.
1,000,000 parts of	Mercury	become	1,018,153	1 in 55	Regnault
„	Water	„	1,046,600	1 in 21·3	Dalton
„	Oil	„	1,080,000	1 in 12·5	
„	Alcohol	„	1,111,000	1 in 9	

It has, however, been found that in many liquids of analogous chemical composition the expansion is very nearly uniform, if the comparison be made, not at the same temperature, but at *corresponding temperatures*, that is to say, at equal distances from the boiling point, the point at which cohesion is just about to yield to the repulsive action of heat. The same thing has also been observed between some liquids which present no analogies in their nature, as was originally observed by Gay-Lussac in comparing the expansion of alcohol and carbonic disulphide. The subject has more recently been investigated with great care by Pierre (*Ann. Chim. Phys.* [3], 1845, xv. 325; 1847, xix. 193; 1847, xx. 5; 1847, xxi. 336; 1851, xxxi. 118) and by Kopp (*Pogg Annal.* 1847, lxxii. 1 and 223; *Liebig's Annal.* 1855, xciii. 157; xciv. 257; and xcv. 303). In most instances there is a very satisfactory agreement between the results obtained by these observers upon the same liquid. Some of their results are embodied in the following table. The volume of each liquid at its boiling point is taken at 10,000. The numbers in the table indicate the volume of the liquid, first at 40° C. below the boiling point of each liquid, and again at a still lower temperature, 70° C. below that point; the most expansible liquids being placed first in the table.

The expansion of the different liquids used in these experiments was determined by enclosing in tubes similar to those employed for thermometers, known volumes of the liquid at a particular temperature, and measuring the expansion experienced in each case, making the necessary correction for the dilatation of the glass envelope. In fact, a number of thermometers were prepared, in each of which one of the various liquids under experiment was substituted as the expansible material in place of mercury.

Expansion of Liquids at Corresponding Temperatures.

10,000 Parts of the following Liquids at their own Boiling Points.	Formula.	Volume at 40° C. or 72° F. below boiling.	Volume at 70°C. or 126°F. below boiling.	Observer.
Ether	$C_4H_{10}O$	9384		P.
Silicic chloride	$SiCl_4$	9390	9027	„
Ethyl chloride	C_2H_5Cl	9419		„
Ethyl acetate	$C_2H_5C_2H_3O_2$	9424	9053	„
Ethyl formiate	$C_2H_5CHO_2$	9430	9064	„
Methyl acetate	$CH_3C_2H_3O_2$	9431	9065	„
Methyl butyrate	$CH_3C_4H_7O_2$	9438	9075	„
Ethyl butyrate	$C_2H_5C_4H_7O_2$	9446	9065	„
Methyl valerate	$CH_3C_5H_9O_2$	9445	9084	Kp.
Methyl bromide	CH_3Br	9438		P.
Ethyl bromide	C_2H_5Br	9452	9091	„
Stannic chloride	$SnCl_4$	9475	9130	„
Phosphorous chloride ...	PCl_3	9484	9157	„
Benzol...	C_6H_6	9486	9145	Kp.
Butyric acid	$HC_4H_7O_2$	9497	9164	„
Acetic acid	$HC_2H_3O_2$	9520	9207	„
Formic acid	$HCHO_2$	9560	9264	„
Methyl iodide	CH_3I	9494	9163	P.
Ethyl iodide	C_2H_5I	9514	9187	„
Dutch liquid	$C_2H_4Cl_2$	9499	9171	„
Monochlorinated hydrochloric ether	C_2H_4Cl,Cl	9481	9121	„
Monochlorinated Dutch liquid	C_2H_3Cl,Cl_2	9518	9191	„
Dichlorinated hydrochloric ether	$C_2H_3Cl_2,Cl$	9451	9094	„
Wood spirit	CH_4O	9488		
Alcohol	C_2H_6O	9536	9225	„
Fusel oil	$C_5H_{12}O$	9503	9192	„
Carbonic disulphide	CS_2	9521	9201	„
Sulphurous ether	$C_3H_{10}SO_3$	9536	9215	„
Bromine	Br	9547	9247	„
Titanic chloride	$TiCl_4$	9553	9247	„
Arsenious chloride	$AsCl_3$	9560	9256	„
Ethylene dibromide	$C_2H_4Br_2$	9562	9264	„
Phosphorous bromide... ...	PBr_3	9620	9353	„
Silicic bromide	$SiBr_4$	9627	9340	„
Water	H_2O	9747	9627	„

In comparing corresponding compounds obtained from wood-spirit and from alcohol (two homologous organic liquids), a remarkable parallelism in their rates of expansion has been observed. The ethyl and methyl acetates correspond closely with each other, and with the butyrates of the same substances. The ethyl and methyl bromides also correspond. So do the ethyl and methyl iodides. Wood-spirit and alcohol do not differ greatly from each other, or from an allied compound produced during fermentation, which has received the name of fusel oil; but the rates of expansion of the homologous butyric, acetic, and formic acids differ rather more widely. Ethyl formiate is metameric with methyl acetate

(that is to say, it is composed, in 100 parts, of the same chemical elements, in precisely the same proportions), and both expand also at exactly the same rate; but this uniformity of expansion in metameric bodies is not always observable: considerable differences are found to exist, for example, between the rates of expansion of the metamerides Dutch liquids and monochlorinated hydrochloric ether, and between monochlorinated Dutch liquid and dichlorinated hydrochloric ether.

Two elements, however, such as chlorine and bromine, which are most closely allied in chemical properties, and which form compounds possessing the same crystalline form, may yet combine with the same element, and produce liquids which have totally different rates of expansion. For instance, Dutch liquid and ethylene dibromide differ considerably, and no correspondence exists between the expansion of silicic bromide and silicic chloride.

(134) *Expansion of Gases.*—When the temperature rises beyond a certain point in liquids, they change their state, cohesion is entirely overcome, repulsion predominates, and the aëriform condition supervenes. Expansion for equal increments of temperature is in gases far greater than in solids or in liquids. If the open extremity of a tube, on the other end of which a bulb is blown, be plunged into water, the heat of the hand will be sufficient to dilate the air in the bulb so as to cause a part of the enclosed air to escape. In gases where cohesion is entirely overcome, no such variety in expansion is exhibited as in the case of liquids and of solids; and it may, without sensible error, be assumed that in gases, and also in vapours at considerable distances above their points of condensation, the rate of expansion is the same in all. From the freezing to the boiling point of water, they increase in volume more than one-third, or $\frac{1}{3\cdot 6}$, 1000 parts at 0° becoming 1367 at 100° C.*

(135) *Thermometers.*—Whether the body be in the solid, the liquid, or the gaseous condition, the change of volume is very nearly proportionate to the change of temperature; and the same body, with the same initial temperature, always expands to the same extent for the same increase of temperature: for example, a body at the temperature of 20° will, however often it be heated to 100°, always expand to the same volume; and on cooling to its original temperature of 20°, it will always return to its original volume.

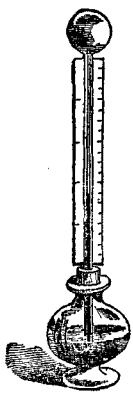
By ascertaining exactly the extent of this expansion, a ready and available measure of temperature is afforded; and accord-

* Regnault (*Ann. Chim. Phys.* 1842 [3], iv. 5 and v. 52) and Magnus (*Ib.* [3], iv. 330) have published independent and elaborate investigations on the expansion which various gases undergo on the application of heat. According to their experiments, the coefficient of expansion is not rigidly uniform for all gases; the expansion being greatest for those which are most readily condensible, whilst for the gases which have resisted all efforts to liquefy them, scarcely any appre-

ingly instruments termed *thermometers* (from θερμὸς, hot, μέτρον, a measure) have been constructed for this purpose.

Air, from the delicacy of its indications, and the regularity of its expansion, would seem to be the material best fitted to measure changes of temperature, and indeed it was the substance first tried. The *air thermometer* consisted simply of a bulb of glass, with a narrow elongated stem dipping into some liquid (fig. 116); as the bulb became heated the air expanded, and depressed the liquid in the stem: as it cooled the air contracted and the liquid rose; a scale attached to the stem gave the amount of the expansion or contraction. But the size of the instrument and the extreme delicacy of its indications limited the range through which it could be employed, and impaired its utility. It was also soon observed that differences of atmospheric pressure, entirely independent of temperature, caused an alteration in the volume of the air: this may be seen by introducing such an instrument under the receiver of an air-pump, and moving the handle; very slight motion causes a great alteration in the height of the column of liquid in the thermometer.* This diffi-

Fig. 116.



ciable differences are observed. The following table contains a summary of the results of these experiments:—

Expansion of Gases by Heat.

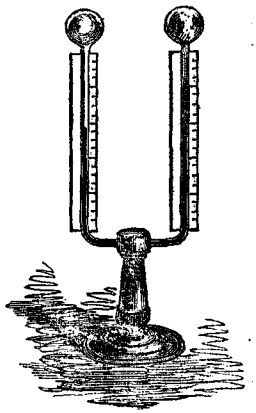
1000 Parts at 0° C. or 32° F. become, (the pressure remaining unaltered)	At 100° C. or 212° F.	
	Regnault.	Magnus.
Hydrogen	1366·13	1365·659
Carbonic oxide	1366·88	
Atmospheric air	1367·06	1366·508
Nitrogen	1366·82	
Hydrochloric acid	1368·12	
Carbonic anhydride	1370·99	1369·087
Nitrous oxide	1371·95	
Cyanogen	1387·67	
Sulphurous anhydride	1390·28	1385·618

For ordinary purposes, sufficient accuracy is, however, attained by assuming the expansion of gases and vapours by heat, between 0° C. and 100°, at $\frac{1}{3}\frac{1}{0}$ of the volume at 0° C.; this is about $\frac{1}{491\cdot4}$ for each degree of Fahrenheit, or $\frac{1}{273}$ for each degree Centigrade, upon the volume occupied by the gas at 32° F. or 0° C.

* The expansion of air, however, when measured with due precaution, gives a more accurate means of estimating temperature than any other mode hitherto devised, but the application of air to this purpose requires elaborate and special contrivances.

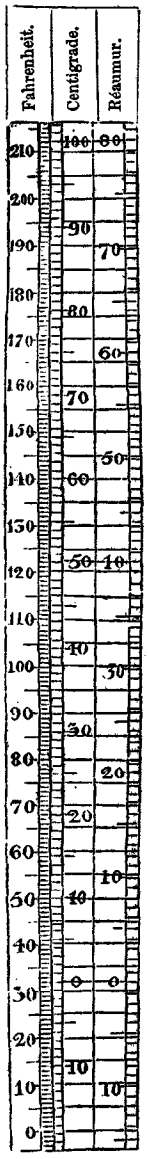
culty was obviated by a modification of the instrument in which atmospheric pressure was altogether excluded; two bulbs were blown at the extremities of a stout tube, which was bent twice at right angles, and a liquid was included in the stem (fig. 117). The instrument in this form, however, would not indicate general changes of temperature, but only differences between the temperature of the two bulbs: if one were warmer than the other, the air expanded in that bulb and drove the liquid in the stem towards the other bulb: it was hence termed the *differential thermometer* or *thermoscope*, and formed, in a limited number of cases, an instrument of great sensitiveness and utility.

FIG. 117.



(136) *Graduation of the Thermometer.*— The next great improvement in the thermometer was made by the Florentine academicians: they substituted the expansion of a liquid for that of air, employing spirit of wine for this purpose, and they divided the stem of the instrument, arbitrarily as before, by means of small dots of enamel, placed at equal distances upon the tube. As the scales of different instruments were not divided upon any uniform principle, the results which they furnished did not admit of direct comparison. This evil was, however, remedied by Newton, who applied Hook's observation, that the melting point of ice always occurs at a fixed temperature; and finding that the boiling point of water under certain standard circumstances is equally constant, he proposed these as fixed points, between which the scale should be divided into a certain number of equal parts; the scale being continued above and below, with similar divisions, as far as might be necessary. Unfortunately, this interval has in different countries been differently subdivided. In England, Fahrenheit's division into 180° has hitherto been principally employed; the zero, or 0°, upon this scale being 32 of these degrees below the freezing point of water. In France, and generally on the Continent, the Centigrade division introduced by Celsius prevails; the interval between the freezing and the boiling points being subdivided into 100°, the degrees being counted upwards and downwards from the freezing point, which is reckoned 0°, the lower temperatures being indicated by the prefix of the negative algebraic sign −.

FIG. 118.



Réaumur, whose division is still used in Germany and Russia, divided the same interval into 80°, making his zero at the freezing point of water.

The conversion of degrees upon one scale into those of another is easily effected by the use of the following formulæ :—

Fahrenheit to Centigrade, $\frac{5}{9}$ $(F°-32)=C°$.
Centigrade to Fahrenheit, $\frac{9}{5}$ $C°+32=F°$.
Réaumur to Fahrenheit, $\frac{9}{4}$ $R°+32=F°$.
Fahrenheit to Réaumur, $\frac{4}{9}$ $(F°-32)=R°$.
Centigrade to Réaumur, $\frac{4}{5}$ $C°=R°$.
Réaumur to Centigrade, $\frac{5}{4}$ $R°=C°$.

The annexed cut (fig. 118) exhibits the three scales placed side by side, and shows the corresponding values through a considerable range of temperature.*

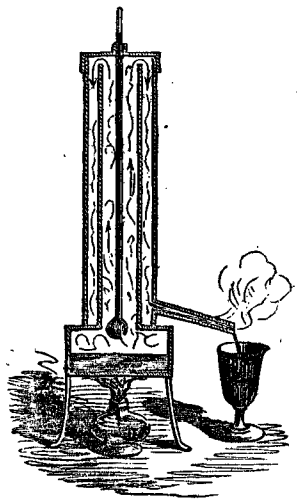
The employment of spirit of wine as the expansible liquid for measuring temperature, is attended with advantages where low temperatures are concerned, inasmuch as spirit of wine has never yet been solidified by cold. But owing to the low temperature at which the spirit boils, it cannot be applied for high ranges of temperature; the heat of boiling water would be sufficient to burst the thermometer, in consequence of the generation of the vapour of alcohol within the instrument. For most purposes mercury is a more convenient thermometric liquid; it embraces a considerable range of temperature, freezing at $-38°{\cdot}8$ C., or $37°{\cdot}9$ below 0° F., and not boiling under 350° C., or 662° F. It has also the advantage of not adhering to the sides of the tubes.

(137) *Tests of a Good Thermometer.*—A good mercurial thermometer should answer to the following tests: when its bulb and stem to the top of the mercurial column are immersed in melting ice, the top of the mercury should indicate exactly 0° C.; when suspended with its bulb and scale immersed in the steam of water boiling in a metallic vessel, as represented in

* A table of the degrees of the Centigrade scale, with their comparative values on that of Fahrenheit, will be found in the Appendix to this volume.

fig. 119 (the barometer standing at $760^{mm.}$), the mercury should remain stationary at 100° C. When the instrument is inverted, the mercury should fill the tube, and fall with a metallic click, thus showing the perfect exclusion of the air. The value of the degrees throughout the tube should be uniform: to ascertain this, a little cylinder of mercury may be detached from the column by a slight jerk, and on inclining the tube it may be made to pass from one portion of the bore to another. If the scale be properly graduated, the column will occupy an equal number of degrees in all parts of the tube.*

FIG. 119.



The expansion of which a thermometer thus takes cognizance is not the entire expansion of the mercury, but the difference between the expansion of the mercury and of the glass; both expand, but the mercury expands the more of the two, and the column of metal therefore rises in the stem of the instrument.

If a thermometer be graduated immediately after it has been sealed, it is liable to undergo a slight alteration in the fixed points of the scale, owing to the gradual contraction of the bulb, which does not attain its permanent dimensions until after a lapse of several months. From this circumstance, the freezing point may be elevated from $\frac{1}{7}$ to $\frac{1}{4}$ a degree C.; and thus the graduations throughout the scale would indicate a temperature higher than the true one by the amount of the error. In some thermometers, even after long use, the bulb, as Despretz and Pierre have shown, after exposure to a heat not exceeding that of boiling water, does not, on cooling, contract at once to its proper dimensions; and thus a temporary displacement of the graduation and depression of the freezing point below the mark, owing to a temporary dilatation of the bulb, is caused every time such instruments are heated to 100° C.

(138) *Different Forms of Thermometer.*—The variety of circumstances under which thermometers are used, necessarily demands a considerable variety in their form. It is desirable,

* In accurate observations, when the column of mercury in the stem of the instrument is exposed to a temperature different from that of the bulb, a correction must be made on this account. If the bulb of the thermometer be placed in the steam of boiling water while the stem projects into the atmosphere, and is of the temperature say of 15° C., an error exceeding 1°·5 C. might easily be made. Wherever it is practicable the whole column of mercury should be raised to the same temperature as the bulb.

for delicate experiments, to reduce the mass of the instrument, in order to diminish the amount of heat required to raise its temperature to that of the bodies with which it is brought into contact; but where minute subdivisions of a degree require notice, it is better to employ a thermometer with a large bulb and a fine bore. A useful form of the instrument is the self-registering *maximum and minimum thermometer*.—The common maximum thermometer, or that of Rutherford, consists of a mercurial thermometer, with a horizontal stem, in the bore of which a small piece of steel wire is included above the mercury. As the mercury expands it pushes the steel before it, and when the mercury contracts, and recedes towards the bulb, the wire does not follow it. The minimum temperature is observed by means of a spirit thermometer, arranged like the mercurial one, but the index consists of a small piece of enamel, sunk below the surface of the liquid column. As the spirit descends, it carries the index with it by capillarity, as soon as the upper extremity of the index reaches the surface of the liquid; but the liquid, on expanding, readily passes by the enamel, and leaves it at the lowest point to which the column had retreated. *Six's thermometer* is constructed upon a somewhat similar principle, but it is less portable, and more liable to derangement. A simpler form of maximum thermometer has been constructed by Negretti and Zambra; it is merely an ordinary thermometer, placed horizontally, with a contraction in the tube, just above the bulb, so that it allows the mercury to pass when it expands, but, owing to the narrowing, the metal does not recede when the temperature falls. It therefore indicates the highest temperature attained since the last observation. In the maximum thermometer of Phillips the index is merely a small portion of the mercurial column itself, which is detached from the rest, and separated from it by a minute bubble of air. In both the forms last mentioned the true place of the mercurial column is restored by placing the instrument vertically, and giving it a slight swinging motion.

In deep-sea soundings in which the temperature was determined by self-registering thermometers, it was found that the pressure acting on the exterior of the bulb produced an elevation of the mercurial column, and recorded temperatures several degrees too high. This has been prevented by blowing another bulb round the thermometer bulb, and nearly filling this with alcohol, the air being removed from the space at the top of the bulb by boiling the spirit before sealing. Any pressure on the

external bulb merely diminishes the space occupied by the alcohol vapour, and is not communicated to the interior bulb. When submitted to hydraulic pressure of three tons on the square inch, the index of one of these protected thermometers was raised 1°·5 F., due to the heat produced by the compression of the water, while an unprotected thermometer indicated a rise of 11°·5 F. (W. A. Miller, *Proc. Roy. Soc.* 1869, xvii. 482).

(139) *Increase of the Rate of Dilatation with Rise of Temperature.*—A scale divided upon the principles already described evidently depends for accuracy on the supposition that equal increments of heat produce equal amounts of expansion. With due precautions, a pound of water, at 0° C., mixed with a pound of water at 100°, should yield a mixture in which the thermometer should stand at 50°, the exact mean. Yet it is not true that even in the same substance equal increments of heat at *different* temperatures produce an equal amount of expansion:—for example, the expansion of mercury for the 10° between 0° and 10°, is less than its expansion for the 10° between 90° and 100°. In the mercurial thermometer, for temperatures between freezing and boiling water, it may nevertheless be assumed, without sensible error, that equal increments of heat raise the thermometer through an equal number of degrees. The increase in the capacity of the glass bulb, especially if the thermometer be made of crown glass, almost exactly compensates for the increasing rate of the expansion of mercury; though for temperatures above 100° the compensation is not so exact. The general result is, that for all bodies, in proportion as the temperature rises, the expansion increases; the distance between the particles augments with the heat, and consequently their mutual cohesion is more readily overcome. The expansion of mercury, for example, for three progressive intervals of 100° C., according to Regnault, is the following: between 0° C. and 100° it is 1 part in 55·09; between 100° C. and 200° it is 1 in 54·57; and between 200° and 300° C. 1 in 54·11. Platinum is more equable in its expansion than any other of the metals, though it also exhibits a similar increase in the rate of its expansion as the heat rises.

The following table embodies some experimental results obtained upon this point by Dulong and Petit:—

Increase of Mean Dilatation in Volume by Heat.

Material employed.	Mean Expansion for each Degree C.			
	Between 0° and 100°.	Between 0° and 200°.	Between 0° and 300°.	Between 0° and 350°.
Glass	1 in 3870	1 in 3630	1 in 3290	
Platinum...	1 in 3770		1 in 3630	
Iron	1 in 2820		1 in 2210	
Copper	1 in 1940		1 in 1770	
Mercury	1 in 5550	1 in 5425	1 in 5300	
Do. (Regnault) ...	1 in 5508	1 in 5433	1 in 5359	1 in 5323
Mercury in glass ...	1 in 6480	1 in 6377	1 in 6318	

The temperature of 572° (300° C.), as measured by an air thermometer, if measured by the expansion of mercury, in an ordinary thermometer, would be indicated as 586° (307°·7 C.), because the apparent dilatation of the mercury increases as the temperature rises.*

In consequence of this expansion of all vessels employed to contain the mercury, there is considerable difficulty in measuring the absolute expansion of mercury; but the difficulty was ingeniously overcome by Dulong and Petit in the following manner (*Ann. Chim. Phys.* 1817 [2], vii. 124):—Two long vertical tubes of glass, open at the upper extremities to the air, were connected below by a capillary tube, and the apparatus was filled with mercury. The mercury in both limbs stood at the same level so long as the temperature of both was equal. One limb of the apparatus was now enclosed in melting ice, whilst the other limb was surrounded by a hot bath, the temperature of which could be regulated at pleasure: the mercury in the heated limb of course expanded with the heat, consequently a longer column of the hot mercury was required to balance a corresponding column of the cold mercury. By means of a cathetometer (*note*, p. 60), the difference in height of the two columns was read off, and the length of each column being known, it was easy to calculate the density of the mercury for any given temperature above the freezing point.

These experiments have been repeated by Regnault on a larger scale, and

* If the specific expansion of each solid and liquid were equal for that substance for equal increments of temperature, the volume of the body might be calculated for any given temperature by the formula $V = 1 + at$, in which V is the required volume, 1 the volume at 0° C., t the temperature in degrees C., and a the coefficient of expansion ascertained by experiment. Thus the volume of mercury for any temperature between 0° C. and 100° C. may be approximately determined by the formula, $V = 1 + 0{\cdot}0001815\,3\,t$; but, generally speaking, it becomes necessary to take other terms of the series into the account, so that the formula becomes

$$V = 1 + at + bt^2 + ct^3,$$

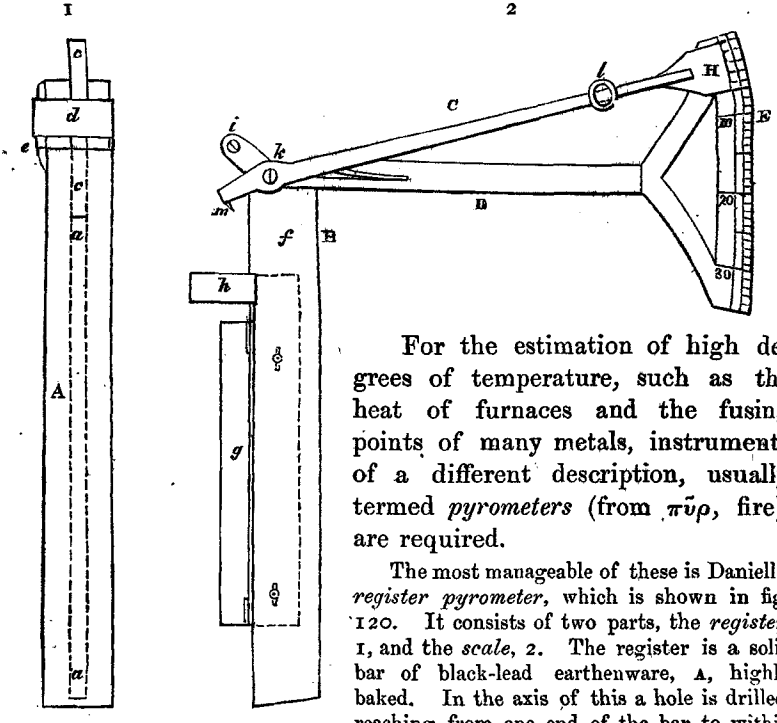
a, b, and c, being coefficients calculated from the experimental numbers.

In the case of permanent gases, the simple formula, $V = 1 + at$ gives the true result for the expansion, the coefficient a being taken = 0·002036 for each 1° F., or = 0·003665 for each 1° C.

with additional precautions: he obtained as the result numbers slightly lower than those of Dulong and Petit.

(140) *Pyrometers.*—Since the expansions of dissimilar metals for equal increments of temperature are unequal, it is evident that if a compound bar, consisting of two such metals as brass and steel, be formed by riveting equal plates of each metal together, the application of heat would occasion curvature of the bar; the concavity being upon the side of the steel, the metal which expands least. On this principle, a very delicate solid thermometer has been constructed by Breguet. It consists of a compound ribbon of three metals, platinum, gold, and silver, which are rolled out into a very thin lamina and coiled into a cylindrical spiral, to the lower extremity of which an index is attached, the upper end of the spiral being fixed. The silver expands much more than the platinum, so that the coil twists and untwists as the temperature rises and falls. The value of the degrees is ascertained by comparison with a standard thermometer.

FIG. 120.



For the estimation of high degrees of temperature, such as the heat of furnaces and the fusing points of many metals, instruments of a different description, usually termed *pyrometers* (from πῦρ, fire), are required.

The most manageable of these is Daniell's *register pyrometer*, which is shown in fig. 120. It consists of two parts, the *register*, 1, and the *scale*, 2. The register is a solid bar of black-lead earthenware, A, highly baked. In the axis of this a hole is drilled, reaching from one end of the bar to within half an inch of the other extremity. In this cylindrical cavity a rod of platinum or of iron, *a*, *a*, $6\frac{1}{2}$ inches long, is placed. Upon the top of the bar rests a cylin-

drical piece of porcelain, *c c*, sufficiently long to project a short distance beyond the extremity of the black-lead bar, so as to serve as an index. It is confined in its position by a ring or strap of platinum, *d*, passing round the top of the black-lead tube, which is partly cut away at the top; the ring is tightened by a wedge of porcelain, *e*. When exposed to a high temperature, the expansion of the metallic rod, *a a*, forces the index forward to a distance equal to the difference in the amount of expansion between the metallic rod and the black-lead bar, and when cool, it will remain protruded to the same distance, which will be greater or less according to the temperature: the exact measurement of this distance is effected by the 'scale,' 2. This scale is independent of the register, and consists of two rules of brass, *f*, *g*, joined together by their edges accurately at a right angle, and fitting square upon the two sides of the black-lead bar. Near one end of this double rule a small brass plate, *h*, projects at a right angle, which, when the instrument is used, is brought down upon the shoulder of the register, formed by the notch cut away for the platinum strap. To the extremity of the rule nearest this brass plate, is attached a moveable arm, D, turning at its fixed extremity upon a centre, *i*, and at the other end carrying an arc of a circle, E, the radius of which is exactly 5 inches, accurately divided into degrees and thirds of a degree. Upon this arm, at the centre, *k*, another lighter arm, C, is made to turn, carrying upon the extremity of its longer limb a vernier, H, which moves on the face of the arc, and subdivides the graduation into minutes. The shorter arm, which is half an inch in length, crosses the centre, and terminates in an obtuse steel point, *m*, turned inwards at a right angle.

To use the instrument, the metallic rod is placed in the register, the index is pressed firmly down upon its extremity, and secured tightly by the platinum strap and the wedge. The position of the index is then read off on the scale, by placing the register in the re-entering angle for its reception, with the cross-piece firmly held against the shoulder, and the steel point, *m*, resting on the top of the index, in a notch cut for it, which coincides with the axis of the rod. A similar observation, made after the instrument has been heated and allowed to cool, gives the value of the expansion. The scale of the pyrometer is compared with that of the mercurial thermometer, by observing the amount of expansion between two fixed points, such as the freezing of water and the boiling of mercury.

(141) A combination of the thermometer with the pyrometer gives a range of temperature extending through wide limits. The means of attaining very elevated temperatures are much more under command than those of procuring great degrees of cold.

The following table gives, in degrees both of Fahrenheit's and of the Centigrade scale, some remarkable points of temperature:—

	° Fah.	° Cen.
Theoretical Zero of Temperature	—459·4	—273
Greatest artificial cold produced by a bath of Nitrous Oxide and Carbonic Disulphide in vacuo (Natterer)	—220	—140
Greatest cold by a bath of Carbonic Anhydride and Ether in vacuo (Faraday)	—166	—110
Greatest natural cold recorded in Arctic expedition (Sabine)	— 56	— 48·8
Nares, 1875-76	— 72	— 57·7

		° Fah.	° Cen.
Mercury freezes		— 37·9	— 38·8
Freezing mixture of Snow and Salt		— 4	— 20
Ice melts		32	0
Maximum Density of Water		39·2	4·0
Mean Temperature of London (Daniell)		49·7	9·8
Blood Heat		98	36·6
Boiling point of Water		212	100
Mercury boils		662	350
Red Heat just visible in the dark	Daniell.	980	526
Silver melts	Daniell.	1873	1023
Cast-Iron melts	Daniell.	2786	1530
Highest heat of Wind Furnace	Daniell.	3280	1805

(142) *Pressure Exerted by Expansion.*—The amount of pressure exerted by a bar when heated or cooled, if its expansion or contraction is prevented, is enormous; for it is equal to that which would be required to elongate or compress a cold bar by mechanical means, by an amount equal to the expansion or contraction which would have occurred if the bar had been free. According to the experiments of Barlow, a bar of malleable iron of a square inch ($25{\cdot}4^{mm.}$) in section, is stretched $\frac{1}{10000}$ of its length by a ton weight (about 1016 kilos.); the same elongation is produced by about 9° C. In this climate a variation of 45° C. between the cold of winter and the heat of summer is frequently experienced. With that range, a wrought iron bar would be elongated $\frac{5}{10000}$ of its length if it is free to expand, or would exert a stress of 5 tons per square inch of section if the expansion is prevented. Calculating upon Joule's data, it may be estimated that the work done by heat in producing the expansion of 1 lb. of iron between 0° and 100° C., during which it would increase about $\frac{1}{280}$ of its volume, would be adequate to lift a weight of 7 tons to the height of 1 foot—that is to say, that in order to drive asunder the particles to an extent sufficient to cause a pound of iron to increase $\frac{1}{280}$ of its volume, an expenditure of work of this enormous amount would be required.

In many instances in the arts this effect is turned to useful account With this view the wheelwright makes the iron tire of his wheels a little smaller in diameter than the rim of the wheel, and applies the tire in a heated state; on cooling, it contracts, and binds the parts firmly together. In rivetting steam-boilers, the rivets are clenched whilst red-hot, in cooling they contract and draw the plates closely together. But, on the other hand, this expansion requires often to be carefully guarded against. Iron clamps built into furnaces frequently destroy, by their expansion and contraction, the masonry which they are intended to support. In long lengths of steam pipe an expansion joint is provided which permits alteration of length. For the same reason, a small interval is left between the ends of the iron bars in laying down a line of rails. Each tube of the Britannia Bridge, across the Menai Straits, is liable, from

changes of temperature, in the course of twenty-four hours, to an elongation and contraction varying from half an inch to three inches (from 12 to 76 millimetres), and a roller bed is provided to allow this expansion to occur freely.

Brittle substances, such as glass and cast-iron, often crack on the sudden application of heat, because a sudden dilatation is produced upon the surface before the heat has time to reach the interior, and thus the cohesion is destroyed. The thicker the plate the greater is its liability to fracture. Sudden cooling, by inducing unequal contraction, has a similar effect.

A knowledge of these effects of expansion explains why the wires of certain metals, such as iron and platinum, may be soldered into glass; whilst other metals, such as silver, gold, or copper, separate and crack out as the joint cools. The expansion of iron or of platinum differs from that of glass by only a very small amount, whereas other metals vary from it greatly, and contract far more in cooling.

(143) *Anomalous Expansion of Water.*—A remarkable exception to the law of contraction by the lowering of temperature, exists in the case of water. Water follows the regular law until it reaches a temperature of about 4° C. (39°·2 F.); then, instead of contracting, it begins to expand, and continues to do so until it reaches the freezing point. About 4° it is at its point of greatest density, and just before it freezes it occupies the same volume as it did at 9° C. If water at 4° C. be taken as 1000, it has a density, at 0° C., of 999·88 (Pierre). From 4° C. water expands regularly as the temperature rises: so that 1000 parts at 0° C. become

At 0° = 1000·00	At 30° = 1004·21	At 70° = 1022·43
4° = 999·88	40° = 1007·61	80° = 1028·73
10° = 1000·14	50° = 1011·93	90° = 1035·58
20° = 1001·67	60° = 1016·86	100° = 1043·03
		(Despretz.)

More recently Kopp (*Pogg. Ann.* 1847, lxxii. 48) has determined the expansion of water with the following results:—

At 0° = 1·000000	At 30° = 1·004064	At 70° = 1·022246
4° = 0·999877	40° = 1·007531	80° = 1·028581
10° = 1·000124	50° = 1·011766	90° = 1·035397
20° = 1·001567	60° = 1·016590	100° = 1·042986

By dissolving common salt in water, the point of maximum density is lowered, and the solution goes on contracting regularly at temperatures considerably below 4°, until, in sea-water, the anomaly disappears, the maximum density occurring according to Despretz at 25°·38 (−3°·68 C.), a temperature below its point of congelation, which the same observer estimates at 28°·62 (−1°·88 C.). Various other salts besides common salt (sodic chloride) have the effect, when dissolved in water, of lowering its point of maximum density; but amongst the numerous liquids examined by Pierre, no other liquid besides water was found thus to expand whilst the temperature was falling.

(144) *Correction of Volume of Gases for Temperature.*—It has been already mentioned that aëriform bodies expand for equal rise of temperature more than either solids or liquids, and that the rates of expansion for all gases and for vapours, at a sufficient distance from their boiling points, may be assumed to be equal and uniform, at all degrees of temperature and under all variations of pressure. It becomes, therefore, a matter of importance to estimate the amount of this expansion in all experiments where the quantities of gases require to be determined, and where their density is to be inferred from measurement of their volume. Provided that the temperature of the gas be known, the calculation is easily made. Experiment has shown that for every degree of temperature upon Fahrenheit's scale, an amount of expansion takes place equal to $\frac{1}{459}$ of the volume that the gas occupied at 0° F.; that is to say, that a quantity of any gas which, at the temperature of 0°, occupies 459 volumes, for every additional degree increases in volume by 1; so that at 1° it will become 460 volumes, at 2° 461, at 40° 499, at 60° 519 volumes. In England, all comparisons of gases are usually referred to the temperature of 60°. Suppose it be required to ascertain the volume which 9·2 cubic inches of coal gas, measured at 70°, would have when reduced to 60°:—Since 459 volumes of any gas at 0° would at 70°, have increased in volume by 70, it would have become 459+70, or 529 volumes. Again, a gas, which at 0° occupied 459 volumes, would, at 60°, occupy a volume equal to 459+60, or 519. The volume, therefore, of any gas at 70° would bear the same ratio to the volume which it would occupy at 60° as 529 does to 519. And hence

$$529 : 519 :: 9{\cdot}2 : x \ (=9{\cdot}026 \text{ cubic inches}).$$

If the gas, instead of being measured at 70°, had been measured at 50°, and it were desired to reduce the 9·2 cubic inches to the standard temperature of 60°; the gas, which occupied 459 volumes at 0°, would have expanded to 459+50, or 509 volumes at 50°. The ratio to the volume at 60°, which would, as before, be 519, is given as follows:—

$$509 : 519 :: 9{\cdot}2 : x \ (=9{\cdot}381 \text{ cubic inches}).$$

In this case, the observed volume is less than the corrected one; before, it was greater.* An additional and independent correc-

* The correction to 0° C. is made on the same principle with equal facility. Suppose the volume of the gas (say 153$^{c.c.}$) to have been measured at 15° C.; required its volume at 0° C. Since the expansion for each 1° C. is $\frac{1}{273}$ of the

tion of the volume of the gas for the deviation of the barometric pressure from the standard (41) is needed after the correction for the temperature has been made.

(145) Liquids and gases immediately adjust their volume to the alteration of temperature; but, according to observations made in the Arctic Expedition, solids do not immediately do so in all cases: it was frequently observed in the metallic scales of many of the instruments, that full contraction did not occur until a concussion had been given to the apparatus; the metal then contracted suddenly and completely.

(146) *Process for taking the Density of Gases.*—The principal corrections required in the delicate operation of taking the density of a gas with accuracy have now been pointed out. Regnault, in his elaborate researches (*Ann. Chim. Phys.* 1845 [3], xiv. 211), has reduced the number of corrections ordinarily required, by counterpoising the globe in which the gas is to be weighed by a second globe of equal size, made of the same glass; a practice which had previously been adopted by Prout, in his careful investigations on the density of the atmosphere. The film of hygroscopic moisture which always adheres to the glass is equal in both globes; and as the volume of air displaced is also equal in both cases, the calculations for its buoyancy may be dispensed with.

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volume at 0° C., 273 volumes at 0° C. would become 273 + 15 = 288 at 15° C.; consequently

$$288 : 273 :: 153 : x\,(= 145{\cdot}03).$$

Or expressing the whole in general terms; for the English standards, if T be the observed temperature ° F., V the corrected volume at 60° F., V' the observed volume, then

$$V = \frac{519\,V'}{459 + T}.$$

For the French standards, if T be the observed temperature in ° C., V the corrected volume at 0° C., then

$$V = \frac{273\,V'}{273 + T}.$$

The following formulæ are more frequently employed:

$$V = V' \frac{1}{1 + {\cdot}002178\ T} \text{ for the Fahrenheit scale,}$$

$$V = V' \frac{1}{1 + {\cdot}003665\ T} \text{ for the Centigrade scale,}$$

in which 0·003665 is the coefficient of expansion of gases for each degree C.; that is, 1 volume of gas at 0° C. becomes 1·003665 at 1°; 1·03665 volumes at 10°; and so on.

The following is a brief description of the method adopted by Regnault:—A balance capable of weighing 1 kilogramme, and sufficiently sensitive to turn with half a milligramme when loaded, is placed upon a chest provided with folding doors, within which the glass globes, each of the capacity of about 10 litres, attached to the scale-pans, are freely suspended. The globe, B, fig. 121, is hermetically sealed; the globe A, for weighing the gases, is provided with a stop-cock; the air is exhausted from A as perfectly as possible, and it is connected with an apparatus which supplies the gas to be weighed, the gas having been carefully purified and dried. The globe is again exhausted very completely, the last portions of air being thus displaced by the gas, and it is a second time filled with the gas; this process must be repeated a third time, and the gas may then be considered to be free from atmospheric air. To avoid the need of any correction for temperature, the globe is this time placed in a vessel with melting ice (fig. 122), in order to cool the gas to 0° C. When the globe is filled with gas, and sufficient time has elapsed for it to acquire the temperature of the ice, the vessel of mercury, M, into which the escape tube dips, is removed, so as to equalize the pressure within the globe with that of the air; the stop-cock is closed, and the globe withdrawn, wiped carefully with a damp cloth, to avoid rendering the surface electric, and it is then suspended to the scale-pan. It is not weighed, however, until after the lapse of a couple of hours, by which time the equilibrium of its temperature with that of the atmosphere is restored, and the production of currents (152) around it is obviated. The weight, W', is then accurately noted; the globe is again plunged in ice, the gas removed by the air-pump, and the pressure of the gas which still remains in it is measured accurately by the gauge attached to the air-pump. The empty globe is again withdrawn from the ice and weighed as before, representing its weight as w; the difference of the two weights (or $W'-w$) will give the weight of a volume of gas the pressure of which is equal to that of the atmosphere, as marked by the observed height, H', of the barometer at the time of the experiment, diminished by the pressure, h, of

FIG. 121.

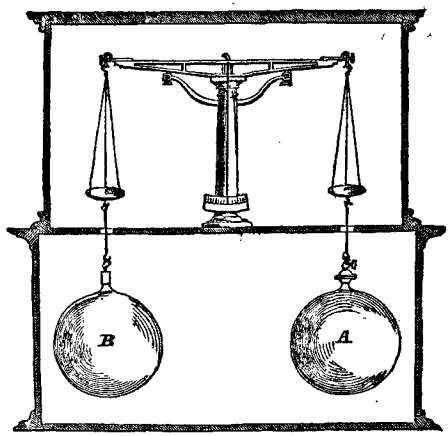
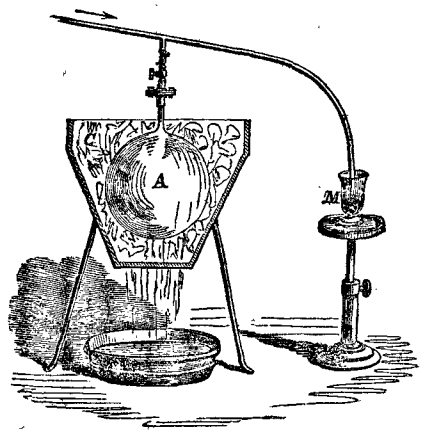


FIG. 122.



the remaining gas, as measured by the gauge. If the capacity of the globe has been previously accurately determined, the corrected weight of the gas will be obtained by the following proportion :—

The observed pressure.		The standard pressure.		The observed weight.		Corrected weight.
$H' - h$	:	H	::	$W' - w$	:	W

Regnault (*Recherches*, etc., *Mem. de l'Institut*, 1847, xxi. 158) has in this manner determined the weights of 1 litre of each of the following gases, at 0° C., and under a pressure of 760$^{mm.}$ of mercury at 0° C. :—

	One litre of			Grammes.
Air,	mean of	9 Expts.*	. . =	1·293187
Oxygen,	„	3 Expts.†	. . =	1·429802
Nitrogen,	„	6 Expts.‡	. . =	1·256167
Hydrogen,	„	3 Expts.§	. . =	0·089578
Carbonic anhydride	„	5 Expts.‖	. . =	1·977414

From these data it is easy to determine the weight of 100 cubic inches of each gas in grains. The litre has a capacity of 61·02704 cubic inches; the gramme is equal to 15·43235 grains; and the expansion of air between 32° and 60° F. by heat is such, that 1,000,000 parts become 1,057,007. The barometric pressure of 760$^{mm.}$ at 0° C. would be equal to a column, at 60° F., of 30·006 inches of mercury. Calculating from these numbers, the weight in grains of the under-mentioned gases under a pressure of 30 inches of mercury (the column being measured at 60° F.) is as follows :—

100 Cubic Inches of	At 32° F.	At 60° F.	Density. Air=1.
	Grains.	Grains.	
Air	32·696	30·938	1·00000
Oxygen	36·150	34·206	1·10563
Nitrogen	31·760	30·052	0·97137
Hydrogen	2·265	2·143	0·06927
Carbonic anhydride ...	49·995	47·307	1·52910

If the amount of condensation which the constituents of a compound gas undergo in the act of combination be known, it is easy to check the experimental determination of its density, and

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* The difference between the highest and lowest of these results did not amount to more than $\frac{1}{2000}$ of the entire weight of the air employed.

† Extreme variation, $\frac{1}{2000}$ of the whole.

‡ Extreme variation, $\frac{1}{2000}$ of the whole.

§ Extreme variation, $\frac{1}{700}$ of the whole.

‖ Extreme variation, $\frac{1}{9700}$ of the whole.

to calculate the density of the resulting compound by the following rule:—

Multiply the density of each of the component gases or vapours by the volume in which it enters into the formation of the compound; add these products together, and divide by the number of volumes produced after condensation has occurred.

Suppose, for example, it be desired to know the density of nitrous oxide, which by direct weighing is found to be 1·52: 2 volumes of this gas are formed by the union of 2 volumes of nitrogen and 1 volume of oxygen:—

Density of nitrogen	=	0·9713	×	2	=	1·9426
Density of oxygen	=	1·1056	×	1	=	1·1056
						2)3·0482
Calculated density of nitrous oxide . .					=	1·5241

Again, the density of ammonia may be calculated as follows, experiment giving it as 0·59: 2 volumes of ammonia contain 1 volume of nitrogen and 3 volumes of hydrogen:—

Density of nitrogen	=	0·9714	×	1	=	0·9714
Density of hydrogen	=	0·06927	×	3	=	0·2078
						2)1·1792
Calculated density of ammonia . . .					=	0·5896

Chemists are now frequently in the habit of referring the densities of gaseous bodies to hydrogen as the standard, instead of to atmospheric air, as formerly. As the densities of the gaseous elements and of the vapours of many of the volatile ones are identical with, or bear a simple relation to, the atomic weight when hydrogen = 1; it is much easier to remember their densities than when that of air is taken as unity. A reference to the table on page 30 will illustrate this point. It will there be seen that the column headed Relative Weight contains the densities of the elements relatively to hydrogen; and that in the case of hydrogen, chlorine, oxygen, nitrogen, sulphur, selenium, and tellurium, the densities and atomic weights are identical. With cadmium, zinc, and mercury the vapour densities are one-half the atomic weights; whilst the vapour densities of phosphorus and arsenic are double the atomic weights.

The rule above given applies with equal force to the calculation of the densities of compounds in the state of vapour relatively to hydrogen: thus, for nitrous oxide—

Density of nitrogen . . .	= 14	× 2	=	28
Density of oxygen	= 16	× 1	=	16
				2)44
Calculated density of nitrous oxide . . .			=	22

That obtained by experiment is 21·965.

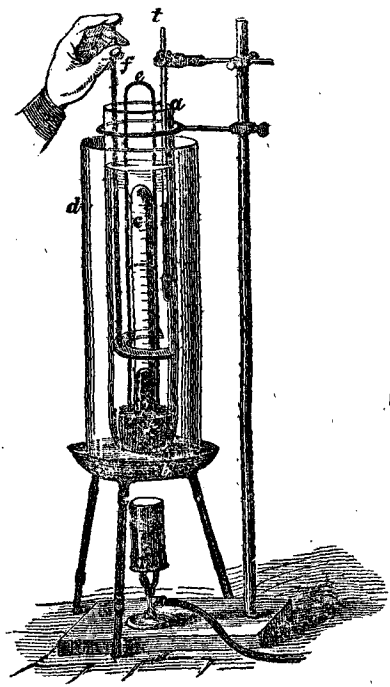
Again, for ammonia—

Density of nitrogen . . .	= 14	× 1	=	14
Density of hydrogen . . .	= 1	× 3	=	3
				2)17
Calculated density of ammonia			=	8·5

Experiment giving 8·526.

(147) *Determination of the Density of Vapours.*—A different method of procedure is required in taking the density of a vapour. This is an operation which the chemist has frequently occasion to perform, as it often throws light upon the composition of the body. Two methods have been proposed for attaining the object; one, devised by Gay-Lussac, is suitable for liquids which boil at temperatures not exceeding 200° C., and it has the advantage of requiring less than a gramme of the substance under trial.

FIG. 123.



Gay-Lussac's method may be practised as follows:—

A known weight of the body for experiment is converted into vapour at a definite temperature, and the volume of the vapour obtained is accurately measured. It is then easy to calculate its density by dividing the weight of the substance by the weight of an equal volume of air at the same temperature and pressure.

The apparatus employed consists of a tall, thin, narrow glass jar, *a*, with a rounded

bottom, which rests upon a small sand-bath. A little mercury is placed in the lower part of the jar, which is then nearly filled with melted spermaceti. Into this tube is introduced a graduated jar, *c*, filled with dry mercury, with a small bulb, of the form shown at *g*, containing the weighed amount of the body, of which the vapour density is required. In order to prevent sudden variations of temperature, the whole is enclosed in a wider glass, *d*, open at top and bottom, and resting on the sand-bath; *e* is an iron spoon, shown separately, which is used to transfer the graduated tube from the mercurial trough to the bath of melted spermaceti; *t* is a thermometer for ascertaining the temperature of this bath, and *f* an agitator for rendering its temperature uniform throughout the liquid.

Having filled the tube *c* with mercury at the mercurial trough, a small bulb destined to contain the liquid for experiment is weighed when empty; it is then completely filled, and weighed a second time: the difference in weight gives the weight of the liquid used. The bulb is next introduced into the graduated tube, and the whole is transferred to the melted spermaceti; the dilatation of the liquid bursts the thin glass of the little bulb, and its contents are converted into vapour. The temperature is gradually raised to a point at least 20° C. above the boiling point of the liquid; the temperature is noted, and the volume occupied by the vapour in the graduated tube is observed. The pressure is next ascertained by measuring the difference in level between the mercury within and without the graduated tube, correcting this column for the temperature, and deducting this corrected height from the observed height of the barometer at the time. Another correction is also required for the column of liquid spermaceti, which must be calculated in its equivalent pressure in mercury, and added to the observed height of the barometer. The following are details of a calculation upon this method:—

Determination of Vapour Density of Ethyl Diethoxalate.

$[C_2H_5,H,C_2(C_2H_5)_2O_3]$ Frankland and Duppa; boiling point 175° C.

EXPERIMENT.

Weight of substance in glass bulb	0·3723 grm.
Observed volume of vapour	100·0 cub. centim.
Temperature of bath	202° C.
Difference of level of mercury within and without the tube	$59^{mm.}$
Height of oil column	$319^{mm.}$
Height of barometer	$763^{mm.}$

CALCULATION.

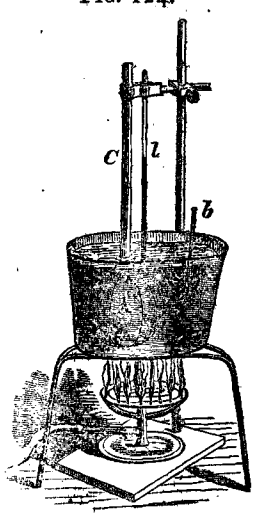
	mm.
Since the mean coefficient of expansion of mercury for 1° C. is 0·000184, between 0° and 200° C., $59^{mm.}$ mercury at 202° would become at 0° C. $\frac{59}{1+(0{\cdot}00184\times202)}$ = ...	56·9
And since the density of melted spermaceti is 0·808, whilst that of mercury at 0° is 13·596, a column of $319^{mm.}$ spermaceti at 202° would be in millimetres of mercury at 0° C. $\frac{319\times808}{13596}$ = . .	19·0
Add this to the observed height of the barometer = .	763·0
	782·0
And deduct corrected height of column of mercury in tube	56·9
We obtain for the true pressure on the vapour in millimetres of mercury at 0°	725·1

Now 100 cub. centim. of vapour measured at 202° and 725·1$^{mm.}$ bar., if they could exist as vapour at 0° C. and 760$^{mm.}$ bar., would = . . .	54·822 cub. cent.
	Grms.
And since 54·822 cub. centim. of the vapour at 0° is 0·3723 grm., 1 litre at 0° would be . .	6·791
But a litre of air is 1·29318 grm. at 0° C. and 760$^{mm.}$ bar., therefore the density of the vapour is $\frac{6·791}{1·29318}$ = ...	5·251

The other method, contrived by Dumas, is applicable to all bodies which boil below the temperature at which glass softens; but it requires a considerable amount of the substance, and if any impurities which have a higher boiling point than the compound under examination be present, they accumulate in the flask and render the apparent weight of the vapour too high. The method of Dumas is as follows:—

A thin glass globe or balloon (A, fig. 124), of 3 or 4 inches (from 7·5 to 10 centimetres) in diameter, is drawn off at the neck into a capillary tube, 5 or 6 inches (12 or 15 centimetres) in length; the open extremity of this tube is attached to a desiccating tube filled with calcic chloride (66), and this is connected with the air-pump. The air is exhausted from the apparatus, and then slowly re-admitted, repeating the process three or four times. By this means any film of moisture which might be adhering to the interior of the globe is removed, and it is filled with air in a dry state: the temperature and pressure of the atmosphere at the time are noted down. The balloon after being detached from the air-pump is accurately weighed; this weight represents that of the balloon and the air which it contains. The capillary tube is then inserted into the liquid which is designed to furnish the vapour the density of which is required: by gently warming the globe, the enclosed air expands, and a small quantity of it is expelled. As the globe cools, the air again contracts and the liquid rises. 8 or 10 grammes of the liquid having been thus introduced, the globe is next firmly attached, by means of copper wire, to a wooden handle, C, and by its means is depressed, as represented in fig. 124, completely beneath the surface of a liquid (water, oil, or zincic chloride, according to the temperature required), which is gradually heated till it is at least 20° or 30° C. above the boiling point of the liquid of which the vapour density is required. The liquid in the globe is thus made to boil briskly, and is converted into vapour, which expels the air and takes its place.

FIG. 124.



After the vapour ceases to escape from the aperture of the capillary tube, the bath is maintained at a steady temperature for a few minutes, to allow the balloon and its contents to acquire the temperature of the liquid in which they are immersed. This temperature is then observed by the thermometer, *l*, and at the same moment the capillary tube is sealed by the flame of the blow-pipe. The balloon is afterwards removed from the bath, and allowed to cool: it is thoroughly cleansed, and a second time accurately weighed. The weight thus

obtained represents that of the balloon with that of the liquid which remained within it in the form of vapour at the moment of the sealing. The capillary neck is now plunged beneath the surface of water (or of mercury), and is then broken off. If the operation be successful, the vapour becomes condensed, and the liquid enters the globe, so as either completely to fill it or to leave only a small bubble of air. The globe, with the water which it contains, is next carefully weighed, and the capacity of the balloon is thus ascertained, since each gramme of water is contained in the space of a cubic centimetre, or 252·4 grains in a cubic inch. The bubble of air is then decanted into a graduated tube, and its volume measured; or the globe may be completely filled up with water and again weighed; the difference of the last two weighings will represent the weight of a volume of water equal to that of the bubble of air.

All the data necessary for calculating the density of the vapour are thus furnished, as will be seen from the following example:—

Determination of the Density of Vapour of Alcohol.

EXPERIMENT.

	Grains.
(1) Weight of the balloon full of dry air, at a pressure of 29·1 inches barometer, and a temperature of 57° F. . .	1187·20
(2) Weight of the balloon full of alcohol vapour, sealed at 212°, barometer at 29·1 inches	1189·20
(3) Weight of the balloon with the water that entered on opening the capillary neck under water	8102·00
	Cubic inch.
(4) Residual air at 57° F.	0·200

CALCULATION.

	Grains.
By (3) the weight of the balloon full of water was . . .	8102·0
By (1) the weight of the balloon full of air was . . .	1187·2
Difference: weight of the water	6914·8
Add $\frac{1}{817}$ for the weight of air displaced by water . . .	8·5
	6923·3
	Cubic inches.
Dividing 6923·3 by 252·4 we obtain, as the capacity of the balloon in cubic inches	27·430
Add to this the volume of the residual air	0·200
(5) The sum gives the capacity of the balloon at 57° . .	27·630*
And the increase of volume due to expansion at 212° . .	0·046
(6) The capacity of the balloon corrected to the temperature of 212° becomes	27·676
27·630 cubic inches of air measured at 57°, with barometer at 29·1 inches, would become at 60° with barometer at 30 inches	26·957

* Where rigid accuracy is desired, it is necessary to calculate the difference between the capacity of the globe at the temperature of the air, and that at the

	Grains.
And would be	8·387
Now (by 1) the weight of the balloon filled with dry air was	1187·20
Deduct the weight of the air	8·39
(7) The difference gives the weight of the empty balloon	1178·81
	Cubic inch.
The 0·2 cubic inch of residual air measured at 57°, and at 29·1 inches barometer, would become at 212° and 29·1 barometer	0·260
	Grain.
(8) And would weigh	0·08
	Cubic inches.
But (by 6) the capacity of the balloon at 212° was	27·676
Deduct dilated residual air	0·260
The difference gives the space occupied by alcohol vapour at 212° and 29·1 barometer	27·416
Now 27·416 cubic inches of vapour, measured at 212° and 29·1 barometer, if they could exist uncondensed as vapour, at 60°, and at 30 inches barometer, would become	20·569
	Grains.
But (by 2) the united weight of the balloon, the vapour, and the residual air was found to be	1189·20
Deduct the weight of the residual air (8)	0·08
The difference gives the weight of the balloon and vapour	1189·12
Deduct the weight of the empty balloon (7)	1178·81
The difference gives the weight of 20·569 cubic inches of alcohol vapour at 60°	10·31

100 cubic inches of alcohol vapour would therefore be 50·123 grains at 60° and 30 inches barometer. Now, 100 cubic inches of air are 30·938 grains, at 60° and 30 inches barometer, therefore 50·123 divided by 31 gives 1·620 as the density of the vapour of alcohol, from the foregoing experiment.

Deville and Troost (*Comptes Rendus*, 1857, xlv. 821, and 1859, xlix. 239) have extended this method of Dumas to the determination of the density of vapours of bodies of very high boiling point. They employ light vessels of porcelain, instead

temperature of sealing, and to add this difference to the capacity as calculated above. When the temperature at sealing is very elevated, this correction acquires some importance; but it is insignificant in most cases, more especially as the vapour densities obtained by experiment never coincide accurately with the theoretical results, and a fair approximation is generally all that is required to indicate the state of condensation of the constituents of the compound. Since the coefficient expansion of flint glass between 32° and 212° F. (0° and 100° C.) is equal to 0·00228366, the increase in capacity of the balloon in the foregoing experiment between 57° and 212° F. is 0·046 cubic inch.

of the glass balloon, and seal the exit tube by means of the oxyhydrogen jet. The constant temperature at which the density of the vapour is determined, is obtained by placing the porcelain vessel in the vapour of a body which boils at a much higher temperature than the substance subjected to experiment; the distillation of the body which furnishes the vapour-bath being conducted in vessels of iron. Boiling mercury, for example, gives a vapour of constant temperature of 662° (350° C.); the vapour of boiling sulphur is estimated at 824° (440° C.); that of cadmium at 1580° (860° C.); and that of zinc at 1904° (1040° C.). But since the determination of these high temperatures is liable to some uncertainty, a comparative experiment is made in a separate porcelain vessel, by employing a substance like iodine, which furnishes a very dense vapour, the density of which at measurable temperatures is exactly known. The experiments thus give the direct relation between the density of the vapour under trial, and that of iodine at the same temperature.

By employing an iron bottle Dewar and Dittmar (*Proc. Roy. Soc.* 1873, xxi. 203) have determined approximately the density of potassium vapour. The interior of the bottle was first deoxidized by heating it to redness, whilst a current of hydrogen was passed into it; it was subsequently placed in a bath of melted zinc, and 200 grammes of pure mercury introduced. When $\frac{3}{4}$ of the mercury had distilled off, an iron test tube, containing 4 or 5 grammes of potassium, was dropped into the bottle, and, after the vapours of potassium had ceased to escape, the orifice of the bottle was closed. When cold, the bottle was opened under water, and the hydrogen produced by the action of the potassium on the water was pumped out by a Sprengel, and measured. In this way it was determined that the vapour of potassium is not more than 45 times as dense as an equal volume of hydrogen, the theoretical density being 39.

§ II. On the equilibrium of temperature.

(148) All bodies, when heated, return sooner or later to the temperature of surrounding objects; the tendency of heat being constantly to preserve or recover an equilibrium. This balance is restored either by the process termed *conduction*, that is, by transmission of heat from particle to particle; or by *convection*, or the motion amongst the particles of liquids or gases; or by *radiation* between bodies at a distance from each other.

Conduction.

(149) If we place the end of a short strip of glass and of a strip of metal, of equal length, in the flame of a lamp, we shall soon be sensible that heat reaches the fingers more rapidly through the metal than through the glass; and shall have a convincing proof that these two substances differ greatly in their rate of conducting heat. Of all known substances, metals possess the greatest conductivity, but even they differ considerably when compared with each other. It may be taken as a rule, although it is liable to numerous exceptions, that the greater the density, the greater the conductivity.

Despretz, many years since, and Langberg, as well as Wiedemann and Franz, have more recently published a series of experiments upon the relative conductivities possessed by different solids. In the experiments of the observers last named (*Pogg. Annal.* 1853, lxxxix. 497), bars of each substance similar in dimensions were exposed at one extremity to a constant source of heat, and the progress of the temperature along each bar was measured, at intervals of 2 inches, by means of a thermo-electric pair. They concluded that the conductivities for heat in metals follows the same order as their electrical conductivities. According to J. D. Forbes, the conductivity of wrought iron for heat diminishes considerably as the temperature rises, and a similar diminution in the conductivities of metals generally for electricity has been ascertained to exist as the temperature rises (276).

Calvert and Johnson (*Phil. Trans.* 1858, 349) have investigated the conductivity of the metals by a still more direct method. Their plan of operating consisted in employing two vessels made of vulcanized caoutchouc, on account of its feeble conductivity. The bars of the metals under trial were each 6 centimetres long, and 1 centimetre square. Each bar in succession was passed through an opening in one of the sides of each vessel into which it projected one-sixth of its length, the intervening portion being covered with vulcanized caoutchouc. A given quantity of cold water sufficient to cover the bar was then introduced into one of these vessels, and the temperature accurately observed; into the other vessel a given quantity of water at about 90° C. was introduced, and the temperature was maintained steadily at this point for 15 minutes by the occasional injection of steam in sufficient quantity. At the end of this time, the temperature of the colder vessel was noted. A comparison of the rise of temperature experienced in this vessel when bars of different metals were employed in succession, furnished the relative conductivities, correction being made for the loss of heat by radiation and transfer from one vessel to the other during the experiment.*

* It is to be regretted that the authors did not test the accuracy of their method by repeating their experiments with bars of the same metals of a dif-

Conductivities for Heat.

Metals Employed.	Calvert and Johnson.		Wiedemann and Franz.
	°C. Rise of Temp.	Mean Conductivity per unit of volume. Silver = 1000.	
Silver	31·90	1000	1000
Gold	31·30	981	532
Gold $\frac{991}{1000}$	26·80	840	
Rolled Copper	26·95	845	736
Cast Copper	25·87	811	
Aluminium	21·20	665	
Rolled Zinc	20·45	641	
Cadmium	18·40	577	
Bar Iron	13·92	436	119
Tin	13·45	422	145
Steel	12·65	397	116
Platinum	12·15	380	84
Sodium	11·65	365	
Cast Iron	11·45	359	
Lead	9·17	287	85
Antimony	6·85	215	
Bismuth	1·95	61	18

The preceding table gives some of the results obtained in this way, compared with those of Wiedemann and Franz.

In the experiments of Calvert and Johnson, the platinum, aluminium, iron, and sodium employed were ordinary commercial samples; the other metals are believed to have been chemically pure. The purity of the metals is indeed a point of great importance, because the presence of small quantities of foreign metals or other substances greatly impairs the conductivity of the mass. It was found, for instance, that gold, when alloyed with 1 per cent. of silver, lost nearly 20 per cent. of its conductivity.

Alloys of tin and lead, and lead and zinc, were ascertained to conduct in the ratio of the mean conductivity of the two metals, and these alloys were found by Matthiessen to conduct electricity in like manner, forming an exception to the generality of the alloys.

Some alloys of good and bad conductors, with the inferior conductor in excess, give a conductivity no higher than that of the inferior metal; bronze, for example, and the alloys $CuSn_2$, $CuSn_3$, conduct no better than tin. The presence of carbon

ferent length—say of ten centimetres; they would no doubt have then obtained the same sequence; but the ratio of the quantities of heat conducted would probably have been different. Their numbers at present must simply be regarded as representing the *order of conductivity*, per unit of volume, not per unit of mass.

diminishes the conductivity of iron. If that of silver be taken as 1000, malleable iron, steel, and cast iron will be represented thus :—

Malleable iron	436
Steel	397
Cast iron	359

It is principally owing to differences in conductivity that bodies at the same temperature excite when touched very different sensations of heat or of cold. A piece of metal feels much hotter or colder than a piece of wood heated to the same degree, because the metal, from its superior conductivity, according as it is above or below the temperature of the hand, imparts heat or receives it more quickly than the wood.

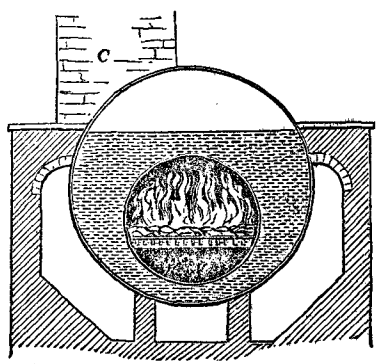
This property of conduction is possessed by liquids in a very limited degree. On filling a test-tube with water, and holding it by the lower part, whilst the top of the tube is placed across the flame of a spirit lamp, the water at the top of the tube may be kept boiling for many minutes without occasioning the slightest inconvenience to the person who holds it. Gases are inferior even to liquids in conductivity ; hence it is that porous bodies, such as wool, fur, and eider-down, which imprison large bodies of air within them, are so well adapted for winter clothing, by preventing the escape of the heat of the body outwards. For the same reason, chiefly, the employment of double doors and windows, which include a layer of air between them, is so useful in preventing the heat of our apartments from escaping outwards; or, as in the case of fire-proof boxes and ice-houses, in preventing that of the outer atmosphere from penetrating. In a similar manner snow preserves the warmth of the earth during the rigour of winter. There seem, however, to be differences in the conductivity even of gases for heat. Magnus considers that the conductivity of hydrogen surpasses that of all other gases, and it is increased by increasing the density of the hydrogen employed. In his experiments he placed a thermometer at the lower part of a glass cylinder, which could be deprived of air, and filled successively with the various gases under trial; the upper part of the cylinder was then heated by means of boiling water. The temperature of the external air was uniformly at 15° C. during the course of the experiment, and care was taken to protect the apparatus from the disturbing influence of radiation; the temperature rose higher when hydrogen was employed than when any other gas was admitted.

The rapid change of particles of air which are in contact with the body, by the action of a wind, renders the human frame much less able to bear cold in a windy than in a still atmosphere. Voyagers in the Arctic regions found that, if properly clad, they could endure in a still air a temperature of $-48°$ C.: while at $-18°$ C. with a brisk wind, it was impossible to face the breeze with safety. A parallel case occurs in liquids: the hand may with impunity be kept stationary in water of a temperature so high, that if the hand were in motion severe pain would be occasioned.

Many familiar contrivances for preventing the escape of heat, and for facilitating the employment of hot bodies, depend upon the use of inferior conductors of heat: for instance, a layer of charcoal is generally interposed between the case of the furnace and its fire-clay lining, in order to confine the heat. The kettle-holder is for this reason used to protect the hand from the heat of the metal; whilst the handles of tea-pots are insulated from the hot metal by non-conducting pieces of ivory. Wicker-work or matting is placed under hot dishes to separate them from the dinner-table by badly conducting substances.

Much of the economy of fuel depends upon a judicious application of these principles. An instructive illustration of their importance is exhibited in the manner in which heat may be economized by an appropriate construction of the boiler of a steam-engine. The form which answers this purpose most perfectly is that which is known as the Cornish boiler. Fig. 125 shows a transverse section of this boiler: it consists of two cylinders placed one within the other; between the two is the space for the water; the interior cylinder contains the fire-grate, ash-pit, and the first portion of the flue: the heat, which would otherwise be conducted away by the fire-bars, and by the masonry of the ash-pit, is thus economized, and the heated products of combustion pass through the boiler for its whole length, which is sometimes as much as 40 or even 60 feet, or from 12 to 18 metres; the hot air then returns along the outside of the boiler towards the fireplace, and once more passes underneath the boiler before it finally reaches the chimney, c. Loss of heat from the outer surface of the boiler is prevented by covering it with a layer of badly conducting material. In the boiler of the locomotive, where a stronger draught is necessary, the fireplace is surrounded at top and on its two sides by a double casing containing water, and the hot air from the furnace passes through the length of the boiler by a number of small tubes, which open at one end into the fireplace, at the other into the chimney. Loss of heat from the external surface is here also prevented by casing the boiler in some non-conducting material, such as felt, which is usually covered with wood.

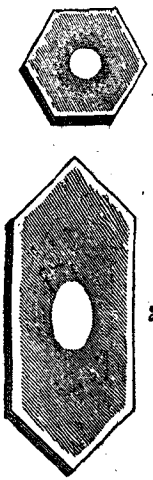
FIG. 125.



(150) *Inequality in the Conductivity in different Directions.*—The researches of De Senarmont (*Ann. Chim. Phys.* 1847 [3], xxi.

457, and 1848, xxii. 179) have shown that although the conductivity of solids which are homogeneous throughout, and of crystals which belong to the regular system, is uniform in every direction, yet that in all crystals which do not belong to the regular system the conductivity varies in different directions, according to the relation of the direction to that of the optic axis of the crystal.

FIG. 126.

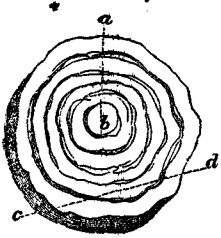


The fundamental fact is easily demonstrated by taking two slices of quartz, one cut parallel to the axis of the prism, the other cut at right angles to that axis; through the centre of each plate a small conical aperture is drilled for the reception of a silver wire, one end of which can be heated in a flame, and which, by its conductivity, acts as an uniform central source of heat. If, previously to the application of heat, the surfaces of the crystal be coated with bees'-wax, the wax on the plate cut across the axis (fig. 126, 1) will be melted in the form of a circle, of which the wire occupies the centre; whilst on the other plate the wax will be melted in the form of an ellipse, the two diameters of which are as 1000 : 1312, the long axis coinciding with the direction of the optic axis of the crystal (fig. 126, 2), showing that the conductivity is greater in this direction than in one at right angles to it: whilst the circular form of the melted wax in the first experiment shows the uniformity with which heat is propagated in all directions around, and perpendicular to the axis of symmetry.

In crystals with two optic axes, the results, although more complicated, present the same intimate connexion with the direction of those lines within the crystal. Bodies which are not crystalline also exhibit an inequality in their conductivity in different directions, when their molecular structure is altered by tension or pressure. Unannealed glass, and plates of glass subjected to compression upon their edges, exhibit these phenomena, the shorter axis of the ellipse being in the line of pressure, or of greatest density.

Delarive and Decandolle have shown that similar differences in conductivity occur in wood, which conducts much better with the grain than across it; that is, better in a direction parallel to the fibres, than across them. Tyndall has not only confirmed this fact, but has also proved that heat passes rather more rapidly in a direction from the external surface towards the centre, *a b* (fig 127), than it does in a direction parallel with the direction of the ligneous rings, *c d* (*Phil. Trans.* 1853, 217); the direction of greatest conductivity coinciding with the direction of

FIG. 127.



greatest porosity and readiest cleavage. The densest woods are not always the best conductors. American birch, though of very small density, conducts better than oak, which is much denser, and far better than ironwood, which has the unusual density of 1·426.

Convection of Heat.

(151) Although the conductivity possessed by liquids and gases is very small, yet they admit of being rapidly heated by a process of circulation or convection, which depends upon the free mobility of the particles that compose them. When heated, each particle expands, and becomes for the time less dense. If the heat be applied at the bottom of a large flask nearly filled with water, into which a little bran has been thrown to enable the eye to follow the motion occasioned, the heated and lighter particles will be seen, by the motion of the bran, to ascend, while their place is supplied by fresh particles from the sides; these in turn come into contact with the heated glass at the bottom, and they again make way for colder portions. An ascending current, as shown in fig. 128, is thus established up the middle, and descending currents flow down the sides of the flask, which are kept cool by the air. Anything that checks this free circulation, and occasions viscosity in the liquid, impedes the distribution of heat. Porridge or starch, during the boiling, requires to be constantly stirred, for the purpose of presenting fresh surfaces to the source of heat, and of preventing the portions in contact with the hot bottom of the vessel from becoming overheated and 'burned.'

FIG. 128.

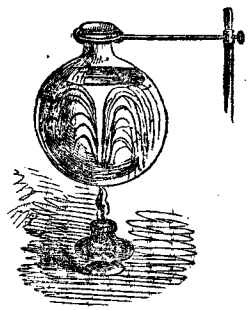
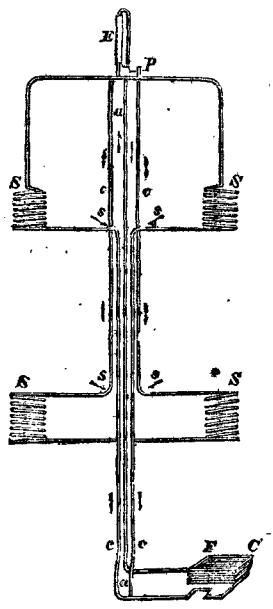


FIG. 129.



The motion thus communicated by heat to liquids, has been ingeniously applied to the warming of buildings, by the circulation of hot water in pipes. One of the most effective methods will be understood by examining fig. 129, which represents Perkins's arrangement for heating by means of hot water at a high pressure. In its simplest form it consists of a continuous wrought-iron pipe, 1 inch (25 millimetres) in diameter ex-

ternally, with a bore half an inch in diameter. The pipe is completely filled with water at P, and closed by a plug. The apparatus is provided with a chamber at E, of about a fifth or a sixth the capacity of the entire tube, to allow for expansion: this chamber being left empty. About a sixth of the entire length of the pipe is coiled up at F C, and is heated by a furnace, which is of necessity placed in the basement of the building. At S S, S S, other coils are formed upon the pipe as it passes through the different apartments which are to be heated. The course of the water is indicated by arrows. The hot water, mixed with bubbles of steam, passes off from the upper part of the fire coil, F C, ascends by the pipe *a a*, to the highest part of the building; it then flows off on either side through the heating coils, S S, S S, and returns by the pipes *c c*, which unite into one before delivering the cooled water to the bottom of the fire coil, F C. *s s*, *s s*, are stop-cocks for arresting the current through any one of the heating coils, S S, S S.

The importance of the exception in the case of water to the regularity of expansion (143), in connexion with these circulatory movements, will now be perceived. During the frosts of winter a rapid process of cooling goes on from the surface of the earth and of our lakes and rivers: the colder water sinks to the bottom, fresh portions being supplied from below, until the whole has reached the temperature of 4° C.; below this point the colder water being the lighter remains at the top, thus protecting the mass beneath from further reduction of temperature by its inferior conductivity, and preventing such a reduction at any considerable depth as would be fatal to the animals which it contains. Ice, too, being lighter than water, floats upon the surface, and thus the bottoms of our rivers are protected from the accumulations of frozen water, otherwise inevitable; and which no subsequent summer heat would ever suffice to melt, or even to reach from the surface. In the ocean, where the maximum of density occurs below 0° C., the depth is so great that, excepting near the polar circles, the low temperature does not last sufficiently long to reduce the entire mass to a degree injurious to animal life.

(152) *Currents in Gases.—Ventilation.*—The motions produced in gases by the expansive action of heat are still more obvious and extensive than those occasioned by it in liquids. The tapering form of flame is due to an expansion of the air, accompanied by a powerful upward current, produced by the heat with which it is attended. A body of heated air confined in a light envelope possesses considerable ascensional power, and constitutes the ordinary fire-balloon; it was, indeed, by means of such a balloon that the first aëronautic excursion on record took place.

The application of the currents produced in air by differences of temperature to the ventilation of our dwellings is a subject of great practical importance. The *draught* produced in the chimney is due to the heat derived from the fire, which dilates the air in

the flue above it, and renders it less dense: it consequently rises in the shaft, and the longer the chimney the more powerful is the draught. Suppose the temperature in the chimney to be on the average of its length 40° above that of the outer air, which may be assumed to be at 7° C.; the dilatation of air for each 1° C. is $\frac{1}{280}$ of its volume at 7° C., the column of air in the chimney will therefore be dilated $\frac{40}{280}$, or $\frac{1}{7}$. A column of such heated air, 8 metres high, which we will assume as the length of the chimney, would therefore only balance a column of 7 metres in height at the temperature of the outer air, and the ascensional force of the heated air would be that due to the difference in weight between the 8 metres of warm air and 8 metres of colder air, or equal to the pressure of a column of the colder air, 1 metre in height. Air must, however, be supplied to the lower opening, in order to allow the equilibrium to be restored; and if the communication of the apartment with the outer air be insufficient (as when the doors and windows are carefully closed, and listed down, to exclude the draughts of cold air that rush in at every crevice to furnish that required to feed the chimney), air will enter at the top of the chimney; just as when a bottle full of air is plunged with its mouth upwards under water, the water enters at the mouth, whilst the air escapes in gushes or bubbles. The consequence of the entrance of cold air at the top of the chimney will be, that such cold air pours down into the room, and, as a necessary result, the chimney smokes. If the door or the window be opened, however, the annoyance ceases. In a room properly ventilated, the requisite supply of fresh air will enter freely, without the necessity of setting the door open.

In ventilating a room, it must be remembered that the air which has been used, and which requires renewal, has become heated by respiration and by the burning of lamps or candles; it therefore rises and accumulates in the upper part of the room. This is easily seen by opening the door of a heated apartment, and holding a candle near the upper part of the doorway; if the window be not open, a current will generally be found blowing the flame from the room. Midway down, the flame will be stationary, while near the floor it will be blown strongly into the room. In this experiment the lighter heated air flows out above, while the denser cold air supplies its place, by entering at the lower part of the room. It is for this reason advisable always to make apertures for the escape of heated air near the ceiling; but it must be remembered that no ventilation can be effectual which does not provide for the entrance of fresh air, which may be previously warmed or not, and which is best admitted at the lower part of the room. In cases where there is a sufficient height of chimney, a contrivance of Dr. Arnott's is a valuable auxiliary to the ventilation; it consists of a balanced valve, opening into the chimney, whilst any momentary downward draught occasioned by the sudden shutting of the door, or otherwise, causes the valve to close, and thus to prevent the escape of smoke into the room.

The velocity of the currents produced by heat, and the rate of cooling effected by them upon a thermometer heated up to a determinate point, vary in different gases, being more rapid the lighter the gas. In hydrogen the rate of cooling is much more rapid than in air, while in carbonic anhydride it is considerably less rapid.

(153) *Trade Winds.*—The processes of circulation produced by heat in liquids and gases, which have just been described, occur upon a vast scale in the atmosphere and in the ocean. The important phenomena of the trade winds arise from movements which originate from these causes. The temperature of the surface of the earth not being uniform, but being highest within the tropics and lowest at the poles, the air near the equator rises in temperature, it becomes expanded, grows less dense, and therefore ascends, its place being supplied by cooler air from the parts adjacent, but nearer to the poles. The heated equatorial air rises to a certain point, and then falls over to supply the place of the cooler air just conveyed from the neighbouring regions. In consequence of these actions, the air upon the surface of the earth is continually moving from the poles towards the equator, and above this current is another proceeding in the contrary direction, from the equator towards the poles. The lower current, which is steadily felt on each side of the equator through at least 30° of latitude, is of the utmost importance to navigation, and forms what are called the *trade winds*. The upper current does not admit of being so accurately traced, but there is satisfactory proof of its existence. The summits of many inter-tropical mountains, such as the Peak of Teneriffe, 12,180 feet (3712 metres) high, and Mouna Kea, in the Sandwich Islands, 18,400 feet (5608 metres) in height, are sufficiently elevated to reach into the upper current; and at the top of these mountains a strong south-westerly wind blows continually, whilst the north-east trade wind is blowing at the base. If the earth were stationary, these currents would set due north and south. The surface of the globe, however, is revolving from west to east, at the average rate of 980 miles per hour in its equatorial part, and the rapidity of motion gradually diminishes towards the poles, at which point the motion almost vanishes. Air, therefore, which flows towards the equator from the poles, is moving more slowly than those regions of the earth towards which it advances. Since, however, the objects upon the surface partake of the motion of the earth at the particular spot on which they rest, and as therefore the earth's motion is not perceptible, the effect of a wind travelling more slowly in the same

direction as that in which the earth is moving would be precisely the same as that of a current blowing in the opposite direction, with a velocity equal to the difference between the rates of the two motions, supposing the earth to be at rest: consequently the wind from the north has a set from the east, which diminishes as it approaches the equator, where the motion of the successive portions of the surface becomes more uniform. From the operation of these causes the north-east is one of the most prevalent winds in our climate. For similar reasons, the equatorial current towards the poles sets in a direction from the west, and retains its course when it comes down to the surface, which it does at and about our latitude, occasioning the westerly winds which prevail in these islands so generally at certain seasons.

The land and sea breezes which occur morning and evening along the coasts of tropical countries, are due to the action of analogous causes. During the early part of the day the surface of the land, from the action of the sun's rays, becomes more heated than the ever-moving ocean; the air above it expands and rises, whilst its place is supplied by cooler air from the ocean—this constitutes the *sea breeze:* whereas in the evening, after sunset, the land cools more rapidly than the ocean, and the air resting upon it contracts in bulk, and becoming heavier, flows out during the night upon the sea, and produces the *land breeze.*

(154) *Gulf Stream.*—Similar currents, of equal constancy and regularity, exist in the ocean, but they are modified in their direction by the general distribution of land and water on the earth's surface. That part of the ocean which is immediately under the tropics, and between the eastern and western hemispheres, for example, becomes highly heated; the water flows off on either side, towards the poles, acquiring a westerly direction as it passes south of the coast of Guinea, and striking the promontory of Cape St. Roque, on the South American coast, is split into two streams; the smaller one continues southwards towards Cape Horn; the larger current maintains a north-westerly course in the Gulf of Mexico, where it receives further accessions of heat, and is gradually changed in its direction; it passes along the southern shores of North America, and finally emerges northward, in the narrow channel between the peninsula of Florida and the Bahama Islands, where it assumes the name of the *Gulf Stream.* The temperature of this current is found to be somewhat above 5° C. higher than that of the neighbouring ocean. The current passes on, gradually widening and becoming less marked, till it is lost on the western shores of Europe. A less accurately defined

under-current, from the poles, is constantly setting in towards the equator, to supply the place of the heated water which takes the course already described. Besides rendering important aid to the navigator, these currents assist in maintaining an equilibrium of temperature on the earth, moderating the severity of the polar frost, and tempering the sultry heats of the tropics. One cause of the comparative mildness of our own winters is the warmth conveyed to our shores by the Gulf Stream.

It would appear from the results of the deep sea soundings in the Atlantic, that there are two currents of water flowing in opposite directions, a warm superficial current passing from the equator towards the poles, and a cold lower current proceeding from the poles towards the equator.

Radiation of Heat.

(155) A person placed in bright sunshine, or before a blazing fire, must perceive that in addition to the gradual mode of propagation from particle to particle, heat is endowed with the faculty of traversing space, and transparent media such as the atmosphere. This transmission of heat occurs in right lines, with a velocity equal to that of light itself; in fact, in this mode of propagation it follows the same laws as light, and like all radiations it diminishes in intensity as the square of the distance from the active centre increases.

The great supply of heat to the earth from the sun is transmitted by the process of radiation. Some idea of the amount of heat thus received by the earth may be formed from a rough calculation made by Faraday, to the effect that the average amount of heat radiated in a summer's day upon each acre of land in the latitude of London, is not less than that which would be emitted in the combustion of sixty sacks of coal. Dr. Siemens (Lecture to British Assoc. Bradford, *Nature*, 1873, viii. 443) calculates that the quantity of heat reaching the earth from the sun is capable of evaporating a layer of water 14 feet in depth annually. This is equivalent to 1680 tons per acre annually, or about 92 cwt. in 24 hours.

Heat, in its radiant state, does not raise the temperature of the media which it traverses: a tube full of ether may be held in the focus of a burning mirror without becoming sensibly hotter; but the moment that the absorption of the rays is caused in any way, as by introducing a bit of charcoal into the liquid, the ether enters into ebullition and is dissipated in vapour.

(156) *Reflection of Heat.*—Polished objects reflect the greater

part of the heat which falls upon them; the reflected and incident rays are always in the same plane, and the angles which they make with a perpendicular to the reflecting surface are always equal. By means of concave mirrors, the rays of heat, like those of light, may be brought to a focus, and, if sufficiently intense, they will ignite combustible substances placed there. The law of the reflection of heat may be roughly demonstrated by holding a flat sheet of tin-plate in such a position before a common fire that the light of the fire may be reflected from it, whilst the observer is screened from the direct rays; the sensation of heat will be perceptible upon the face the moment that the reflection of the fire is seen. The same effect may be shown in a still more striking manner by means of two similar concave parabolic mirrors (fig. 131, page 330) arranged opposite each other, at the distance of 4 or 5 metres or more. If a lighted candle be placed in the focus of one of the mirrors, the rays will fall upon its concave surface, and thence be reflected in parallel lines to the surface of the second mirror, from which they will be a second time reflected, and will converge at its focus; a luminous spot being formed upon a piece of paper held in this position. If for this paper one of the balls of a differential thermoscope (135) be substituted, the expansion of the air in that bulb will afford evidence that the heat as well as the light is reflected. That the rays take the course described, and which is represented in the diagram, and that they do not act upon the instrument by direct radiation, is shown by interposing a small tin-plate screen between the second mirror and the thermometer: in this case the liquid immediately becomes stationary; while, if the screen be placed between the instrument and the candle, no sensible effect is produced.

If, instead of a candle, a red-hot ball be placed in the focus of the first mirror, paper may be scorched, and gunpowder or phosphorus inflamed in the focus of the second. Heat, however, is emitted in the form of rays from bodies, whether such bodies be luminous or not. A canister of boiling water may be substituted for the candle or the red-hot ball, and the heat which it emits, although less intense, will be concentrated by the opposite mirror equally well.

(157) *Absorption of Heat.*—Different substances reflect heat unequally. Polished metals possess the power of reflection in the highest degree, but even the metals differ considerably in reflecting power. Melloni, from his experiments, has concluded that of 100 rays, silver reflects 90; bright lead reflects 60; whilst glass reflects but 10.

If the surface of a body be scratched it reflects heat irregularly, in the same way that a sheet of white paper scatters the light which it reflects; and if the surface be coated more or less completely with lamp-black, the amount of heat which is reflected may be diminished in a degree proportioned to the alteration of the surface. In this case, that portion of the heat which is not reflected is absorbed. When the heat is all reflected, the temperature of the body remains unaltered; but when absorption takes place, the temperature rises in proportion to the quantity of heat which is absorbed.

This difference may be exhibited by placing a lighted taper in the focus of one of the mirrors, and employing in the second focus a differential thermoscope, one ball of which is gilt, and the other ball covered with lamp-black. On placing the gilt ball in the focus, scarcely any motion of the liquid in the stem is perceived; but, on reversing the balls, although the amount of heat which falls on the instrument is no greater than before, the liquid descends rapidly: in the first case, the heat is for the most part reflected: in the second it is absorbed, and the temperature consequently rises.

A similar result may be obtained by taking two bright tin plates, and coating one surface of one of them with lamp-black. On placing them in a vertical position, with a hot iron ball midway between the two plates but not touching either of them, the blackened surface being directed towards the source of heat, it will be found that the blackened plate becomes heated by absorption, while the other remains cool: this may be shown by causing a cork to adhere to the outer surface of each plate, by means of a little wax or pomatum; the wax will melt upon the blackened plate, and the cork will fall from it much sooner than from the bright one.

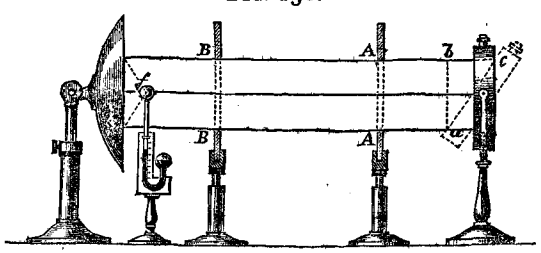
The power of reflection seems to reside almost exclusively in the surface of the body. A film of gold leaf, not exceeding $\frac{1}{8000}$ millimetre in thickness, answers the purpose of a reflector nearly as well as a mass of solid gold; since a sheet of paper partially gilt, if held within a short distance of a mass of red-hot metal, will become scorched, excepting in those parts which are protected by the metallic film. The absorbing power of a substance is complementary to its power of reflecting heat; the best reflectors are the worst absorbents, and *vice versâ*. As is the case with light, so it is found with radiant heat, that, excepting in the case of polished metals, the greater the angle of incidence the more complete is the reflection.

(158) *Connexion between Absorption and Radiation.*—The experiments of Leslie have proved the existence of an important connexion between the absorbing and the radiating powers of the same substance: they are in all cases directly proportioned to each other. The great diversity of radiating power possessed by different substances may be exemplified by the following experiments. Let a cubic canister of tin-plate have one of its sides

covered with lamp-black, and a second side with writing-paper, let a third be scratched in various directions, and let the fourth remain polished. On placing the canister, filled with hot water, in the focus of one mirror, and a thermoscope in the focus of the other, it will be found, on presenting each side in succession to the mirror, that a different temperature is indicated. The heat radiated will be found to be greatest from the lamp-black, less from the paper, still less from the scratched face, and least of all from the polished surface. In consequence of the more rapid radiation from blackened than from polished surfaces of the same metal, a given quantity of a hot liquid placed in a blackened vessel will reach the temperature of the surrounding air sooner than if it be placed in a vessel similar in size and shape, but with a polished surface.

The amount of heat radiated from the surface of an object destitute of reflecting power varies with the angle; the intensity being proportioned to the cosine of the angle which the issuing rays form with the perpendicular to the surface. This fact was proved experimentally by Leslie.

FIG. 130.



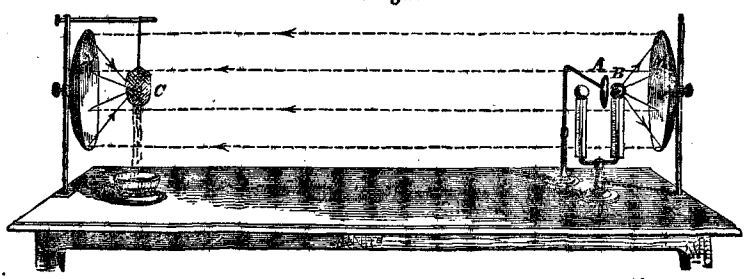
Opposite to a concave mirror he placed a vessel with flat sides filled with boiling water, the side of the vessel next the mirror being coated with lamp-black. Two screens, A A, B B, pierced with apertures of equal size, were interposed between the mirror and the heated vessel, and in the focus of the mirror was placed the blackened ball, *f*, of a thermoscope; no alteration in the indication of the thermometer was produced by varying the inclination of the vessel. The dotted line *a b* represents the extent of the radiating surface when the vessel is vertical. And it is obvious that as the obliquity of the surface *a c* is increased a larger extent of radiating surface is exposed to the thermometer, so that the intensity of the emitted ray must be inversely as the extent of surface in the two cases.

In the economic applications of heat, constant scope is afforded for the employment of the powers of reflection, radiation, and absorption. The meat-screen and the Dutch oven, when kept bright, afford instances of the application of the reflection of heat to beneficial purposes, in directing the heat upon the objects

between them and the fire. Tea made in a silver teapot, which owing to its polished surface long retains its high temperature, is superior in flavour to that made in black earthenware, which rapidly loses its heat by radiation. Pipes for the conveyance of steam should be kept bright until they reach the apartment where the heat is to be distributed, and there the surface should be blackened, in order to favour the process of radiation.

(159) *Formation of Dew.*—The distribution of heat by radiation is not confined to bodies highly heated. All substances, whatever be their temperature, are constantly radiating a certain portion of heat, the amount of which depends upon their temperature. If the different bodies are all at the same temperature, each absorbs from surrounding objects in a given time exactly as much heat as it radiates towards them in the same time. But suppose the bulb of a thermometer to be placed in the focus of a small parabolic mirror, which is turned towards a perfectly cloudless sky, in such a direction that the sun's rays shall not fall upon the mirror, the temperature will sink several degrees; at night, frequently as much as 8° or 10° C. The thermometer, like all other objects, is constantly radiating heat: the mirror cuts it off from the rays proceeding from surrounding objects, and the portion of space towards which it is presented not returning the heat radiated towards it from the instrument, the

FIG. 131.



temperature of the thermometer necessarily falls. A similar experiment is easily made with the conjugate mirrors. If in the focus of one mirror, a cage filled with ice (C, fig. 131) be supported, and in the focus of the opposite mirror, the bulb, B, of the differential thermoscope, which has been blackened to favour radiation, and which is screened from the radiation of surrounding objects by a second small mirror, placed as at A, the liquid will soon rise in the stem connected with the blackened bulb, because the bulb radiates towards the ice, which only partially returns the rays that it receives; and the radiation from sur-

rounding bodies upon the thermoscope being prevented, its temperature falls.*

The principles of radiation were happily applied by Wells to the explanation of the phenomenon of dew. Dew is formed most copiously during a calm, clear night succeeding a hot day: it is deposited in exposed situations and upon the leaves of plants and on filamentous objects in general. As soon as the sun dips below the horizon, and in shady places even before sunset, radiation from the earth is no longer compensated by the solar rays: the temperature of the surface is, therefore, speedily reduced below that of the stratum of air in contact with it; this stratum being charged with moisture, is no longer able to support so much water in the gaseous form, but deposits it (just as when a glass of cold spring water is brought into a warm and moist room, it becomes bedewed with moisture on its outside); and the cohesion collects the water into the pearly drops that stud the herbage and sparkle in the sloping rays of the sun. On cloudy nights little or no dew is deposited, because the masses of suspended water intercept the rays from the earth, and return them to its surface. Overhanging buildings, or the projecting branches of trees, in a similar way, return the heat to the objects beneath them, and prevent the reduction of temperature which necessarily precedes the deposition of dew. On windy nights the equilibrium is rapidly restored by the contact of fresh surfaces of air with the radiating crust of the earth, and little or no dew is formed. Upon metallic bodies, which are bad radiators, and upon the hard-beaten path or road, where the heat is conducted rapidly from the strata beneath, scarcely any dew is deposited; while upon the branching shrub, the tufted grass, and the downy leaf, abundance of moisture is collected, these being precisely the objects which derive most benefit from its presence.

In India, near the town of Hoogly, about forty miles from Calcutta, the principle of radiation is applied to the artificial production of ice. Flat shallow excavations, from one to two feet in depth, are loosely lined with rice straw, or some similar bad conductor of heat, and upon the surface of this layer are placed shallow pans of porous earthenware, filled with water to the depth of one or two inches. Radiation rapidly reduces the temperature below the freezing point, and ice is formed in thin crusts, which are removed as they are produced, and stored away in suitable

* For a discussion of the theory of exchanges the reader may consult Stewart's *Elementary Treatise on Heat*, 2nd ed. 1871, 189, *et seq.*

ice-houses until night, when the ice is conveyed in boats to Calcutta. Winter is the ice-making season—viz., from the end of November to the middle of February.*

The fundamental fact of cooling by radiation of the bodies on which dew is being formed, is easily verified. If a thermometer be laid upon a grass-plat, on a clear night, it will be found to indicate a temperature several degrees below that shown by a second thermometer, suspended a metre or more from the surface.

(160) *Law of Cooling by Radiation.*—The rapidity of the cooling of any body by radiation depends upon the excess of its temperature over that of the external air. The hotter the body, the more rapidly does it cool; and as it approaches the temperature of the air, the more slowly does it lose its excess of heat.

Newton assumed that the quantity of heat lost by a hot body for equal intervals of time, was proportioned to the excess of its temperature above that of the surrounding air; so that if a body heated to 100° in an atmosphere of 0°, lose 10° in one minute, the same body heated to 50° would lose 5° per minute, the air being also at 0°. Later experiments, however, have shown that this assumption is not exact, even for low temperatures, and that it becomes very inaccurate at high ones.

An admirable series of researches upon the rate of cooling by radiation was made by Dulong and Petit (*Ann. Chim. Phys.* 1817 [2], vii. 337). They employed a hollow sphere of thin brass, blackened in the interior, and furnished with arrangements for exhausting it of air. For the heated body they used a thermometer with a large bulb, heated to a determinate degree, and supported in the centre of the hollow sphere. They then placed the apparatus in water which was maintained at a constant temperature, and they observed that the rate of cooling differed with

* A curious formation of ice at the bottom of some rapid, clear, and rocky streams is occasionally seen under the influence of radiation, during the prevalence of bright frosty weather. Ice thus formed is termed *ground-ice*. The water cools down to 39°·2 F. (4° C.) as usual, but below this point the colder water no longer forms a protecting layer, as in still sheets or gently moving streams; the agitation produced by the passage of the water through its precipitous and irregular channel makes the temperature uniform throughout, till it arrives at the freezing point. Angularities and points, under all circumstances, favour the deposition of crystals, and to the irregular surfaces of the rocky fragments in the bed of the stream the ice attaches itself in silvery, cauliflower-shaped, spongy masses, sometimes accumulating in quantity sufficient to dam up the stream, and cause it to overflow; at others, as the ice increases in volume and buoyancy, it rises in large flakes, raising to the surface portions of rock, and even iron itself.

the nature of the gaseous medium contained in the globe. If the temperature of the sphere continued constant whilst the experiments were made *in vacuo* upon the heated body at temperatures ascending according to the terms of an arithmetic progression, the rapidity of cooling increased according to the terms of a geometric progression, diminished by a constant quantity; this constant quantity being the heat radiated back upon the cooling body, from the inner surface of the sphere. If the temperature of the sphere and that of the heated body were *both* raised according to the terms of an arithmetic progression, so that the difference between the two was always constant, it was found that the rate of cooling increased as the temperature rose, according to the terms of a geometric progression.

(161) *Relative Absorbability of Different Kinds of Heat.*—The transmission of radiant heat takes place more freely *in vacuo* than in air. The absorption of heat is, moreover, influenced by an important cause, to which no allusion has yet been made, and which was first placed in its true light by the experiments of Melloni (*Ann. Chim. Phys.* 1831 [2], xlviii. 385; 1833, liii. 5, and lv. 337). It may be illustrated in the following manner:—

If a number of sources of heat be employed, each different in kind and intensity,—such as the naked flame of an oil lamp, a platinum wire heated to redness in the flame of a spirit lamp, a sheet of copper heated to about 400° C. in a current of heated air which is rising from a lamp placed beneath it, and a copper canister filled with boiling water,—the face of a thermoscope covered with lamp-black may be placed at such a distance from each of these sources of heat that the liquid shall stand in each case at the same point; that is, the temperature to which the thermoscope is exposed shall be equal in each case. Now, if these distances be noted, and if the face of the thermoscope be covered with a variety of other substances in succession, instead of with lamp-black, the thermoscope when exposed to each of the different sources of heat in succession, will appear to receive different quantities of heat, although placed at the distances at which, when it was coated with lamp-black, the heat appeared to be equal. Thus, suppose that the heat absorbed, when the lamp-black was used, in each case were equal to 100: if the thermoscope were coated with white-lead, it was found that, at the same distance from the naked flame as before, it indicated a heat of only 53; opposite to the red-hot platinum the heat was 56, instead of 100 as with the lamp-black: with the copper at 400° C., a heat of 89 instead of 100 was indicated; while opposite the

canister of boiling water the thermoscope showed a heat of 100, corresponding exactly with the effect upon it when lamp-black was used.

The following table exhibits some of the results which Melloni obtained by operating in this way:—

Relative Absorbability of Different Kinds of Heat.

Absorbing Surface.	Naked flame.	Incandescent Platinum.	Copper at 752° F. (400° C.)	Copper at 212° F. (100° C.)
Lamp-black	100	100	100	100
White Lead	53	56	89	100
Isinglass	52	54	84	91
Indian Ink	96	95	87	85
Shell Lac...	43	47	70	72
Polished Metal	14	13·5	13	13

Lamp-black appears to absorb all the rays that fall upon it, from whatever source they may have originated; and the amount absorbed by metallic surfaces, although smaller is nearly uniform, whatever be the source. It has also been observed, that the less intense the source of heat, the greater usually is the proportion absorbed.

Franklin, nearly a century ago, made the observation, that solar heat is absorbed with greater or less facility according to the colour of the object upon which the rays fall, but that little or no such difference exists with the heat of a lamp or of a candle. He took pieces of cloth, similar in texture and size, but different in colour, and placed them in the sunlight, upon newly-fallen snow, and he found that the snow melted under the pieces of cloth with greater rapidity the darker the tint—the absorption being greatest with the piece of black cloth, then followed the blue, then the green, purple, red, yellow, and white pieces, in the order enumerated. These effects are due, as Tyndall has shown, not to the colour of the object, but to the nature of the material used as the colouring agent.

(162) *Transmission of Heat through Screens.*—The cause of these remarkable differences will be best understood by a consideration of the phenomena attending the transmission of heat through bodies which allow it to pass unobstructed, as glass allows light to pass. Melloni terms those bodies which thus transmit heat *diathermanous,* or *diathermic* (from διὰ, through, and θερμὸς, hot)—those which do not allow this transmission of heat being termed *athermanous* or *adiathermic.*

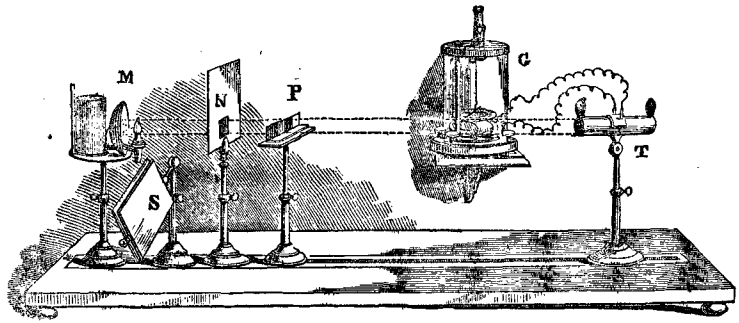
Bodies that are transparent to light are by no means equally so to radiant heat. This arises from two causes, which require to be carefully distinguished from each other, and which may be separately illustrated by a parallel action on the rays of light. A glass containing pure water absorbs very little light, and transmits almost all that it does not reflect: if the attempt be made to measure its transparency by ascertaining the distance at which a page printed in small type is legible when the vessel of water is interposed, and afterwards, when it is removed, the difference in the two cases is hardly appreciable. If a few drops of a mixture of Indian ink and water be added, the transparency will be diminished, and the characters will be legible at a smaller distance; a further addition of ink will diminish the transparency more and more, until the letters can be no longer discerned. The light that is transmitted, however, although diminished in quantity, possesses the same character as the incident light; and a prismatic analysis shows that both consist of the same colours in the same proportion: if in this experiment indigo be substituted for Indian ink, the legibility of the page is diminished to an extent nearly equal; but the prism shows that certain of the rays have been absorbed more completely than others. Similar effects are produced with the rays of heat. There are, however, many substances which are almost perfectly transparent to light—viz., among solids, glass, diamond, Iceland spar, ice, and a great number of crystals; amongst liquids, water, spirit of wine, ether, oil of turpentin, and a multitude of other bodies; and among aëriform bodies, atmospheric air, and the greater number of gases. For heat, on the contrary, there is only one known solid that approaches perfect *diathermancy*, and that is rock salt; many colourless gases possess the property also in a still higher degree; but no liquid has yet been discovered which is free from absorptive action on the thermic rays.

The more important parts of the apparatus employed by Melloni in these researches are represented in fig. 132. One of his four principal sources of heat—viz., naked flame, ignited platinum, blackened copper, heated to 400° C., or copper heated to 100°, was placed at M, on a movable support, behind the perforated screen, N; the rays being concentrated, when necessary, by the concave mirror, M; they were received at a suitable distance from this upon the thermoscope or thermo-multiplier, T.* If a double screen, S, of polished copper were interposed between the source of heat and the thermoscope, the rays of heat were entirely intercepted. Having placed the thermoscope at such a distance as always to indicate, when the copper screens were removed, a constant elevation of

* In these inquiries a peculiar and very delicate thermometric apparatus, termed a *thermo-multiplier* (317), was generally employed.

temperature, a plate of some substance, the diathermancy of which was to be ascertained, was then introduced at P; and on observing the difference of temperature, as marked by the instrument, the portion of heat which the plate transmitted was at once ascertained.

FIG. 132.



In this manner Melloni found that plates of rock salt of great transparency, varying in thickness from $0{\cdot}2^{mm.}$ to 4 or 5 centimetres, transmitted 92 out of every 100 rays incident upon them, whatever were the source of heat employed; the loss of 8 per cent. being mainly due to a uniform quantity which is reflected at the two surfaces of the plate; rock salt, therefore, is to heat what pure colourless glass is to light. The following experiment shows the independence of diathermancy and transparency:—If a cast-iron ball heated to about 200° C. be placed midway between the blackened bulbs of a thermoscope, each bulb will receive an equal amount of heat, and the liquid will remain stationary; but if a plate of rock salt be interposed between the iron and one of the bulbs, and a plate of glass of equal thickness be placed between the hot ball and the other bulb, it will be found that although both plates are almost equally transparent to light, yet the bulb next the rock salt will rise in temperature much more rapidly than the one next the glass. In liquids, the independence of transparency and diathermancy is still more striking. For example, out of 100 rays that fell from an argand lamp, on each of four liquids equally transparent—viz., water, sulphuric acid, ether, and oil of turpentin, water transmitted only 11, sulphuric acid 17, ether 21, and oil of turpentin 31; while chloride of sulphur, which is of a reddish colour, allowed 63 of the incident rays to pass.

The following table includes some of the results obtained by Melloni, for several solid bodies: in these experiments plates of equal thickness were used in each case. (*Thermochrôse*, 1850, Part I. 163, 164.)

Diathermancy of Different Solids.

Each plate was 2·6 mm. or 0·102 inch thick.	Naked Flame.	Ignited Platinum.	Copper 752° F. (400° C.)	Copper 212° F. (100° C.)
Rock salt (limpid)	92·3	92·3	92·3	92·3
Sicilian sulphur (yellow)	74	77	60	54
Fluor spar (limpid)	72	69	42	33
Fluor spar (greenish)	46	38	24	20
Rock salt (cloudy)	65	65	65	65
Beryl (greenish yellow)	54	23	13	0
Iceland spar (limpid)	39	28	6	0
Plate glass...	39	24	6	0
Quartz (limpid)...	38	28	6	3
Quartz (smoky)...	37	28	6	3
White topaz	33	24	4	0
Baric sulphate	24	18	3	0
Tourmaline (dark green)	18	16	3	0
Citric acid	11	2	0	0
Alum	9	2	0	0
Sugar candy (limpid)	8	1	0	0
Ice	6	0·5	0	0

Diathermancy of Liquids contained in Glass—stratum of liquid 9·2 millimetres. The source of heat in each case was an argand oil lamp.

Carbonic disulphide (colourless)	63	Ether	21
Chloride of sulphur (red brown)	63	Sulphuric acid (colourless)	17
Phosphorous trichloride	62	Nordhausen sulphuric acid (brown)	17
Essence of turpentin	31	Nitric acid	15
Colza oil (yellow)	30	Alcohol	15
Olive oil (greenish)	30	Distilled water	11

Tyndall (*Phil. Trans.* 1864, 225) enclosed a certain number of liquids in a cell with sides formed of rock salt, and subjected them to the radiation of a glowing platinum wire. If the amount of heat rays which fell upon the surface of the pile when the empty cell was interposed be called 100, the portion of heat transmitted by the undermentioned liquids was the following:—

Carbonic disulphide	CS_2	83
Do. do. saturated with sulphur ...		82
Do. do. saturated with iodine ...		81
Bromine		77
Chloroform	$CHCl_3$	73
Methyl iodide	CH_3I	69
Benzol	C_6H_6	60
Ethyl iodide	C_2H_5I	57
Amylene	C_5H_{10}	50
Ether...	$(C_2H_5)_2O$	41
Ethyl acetate	$C_2H_5,C_2H_3O_2$	34
Ethyl formiate	C_2H_5,CHO_2	33
Alcohol	C_2H_6O	30
Water saturated with rock salt		26

(163) *Diathermancy of Gases and Vapours.*—The experiments of Knoblauch have shown that even metallic bodies in very thin films are diathermic, presenting in this respect an analogy with their limited transparency to light in films of similar tenuity. Gold and silver transmit certain of the rays of heat more freely than others, whilst platinum appears to transmit all the rays with nearly equal facility. On the other hand, Tyndall (*Phil. Trans.* 1861, 1, and 1862, 59) has found that the gases exert different degrees of absorptive action on the rays of heat, and even when colourless that this effect is strongly marked. Coal gas, for example, exerts a much stronger absorptive effect than atmospheric air, and the vapour of ether considerably more than that of the carbonic disulphide. Rays of certain degrees of refrangibility also are more powerfully absorbed by the colourless gases than others. For example, coal gas arrests the heat-rays from a source below a visible red heat, much more perfectly than it absorbs the rays of the lime light after they have traversed a thin layer of water.*

The following table is given by Tyndall as representing the relative absorptive power for heat emanating from a source at 212° F., of various gases at the normal pressure of 30 inches of mercury, when a column of the gas, 4 feet in length, was subjected to experiment:—

* In conducting these experiments, an arrangement of apparatus was ultimately adopted by Tyndall, the principle of which will be understood from the following description:—The gases which were to be submitted to experiment were placed in a brass tube four feet long, and polished in the interior; but for particular gases a glass tube was substituted. In either case it was closed air-tight at each end by a polished plate of rock-salt, and was connected with an air-pump, so that at pleasure it might be used when exhausted of air, or when filled with different gases in succession. The source of heat employed in most cases was a cube of copper filled with water, which was kept boiling. The face of the cube was turned towards the tube for experiment, and was coated with lamp-black. At the other end of the brass tube, a thermo-electric pile (317) was placed; one face of the pile was directed towards the tube which contained the gas under trial, whilst the other end was directed towards a second cube also containing boiling water. The thermo-electric pile was connected with a very sensitive galvanometer. The experiment was commenced by exhausting the long tube of air, and then adjusting the distance of the second cube of boiling water, interposing or withdrawing a screen until the amount of heat which fell upon the two surfaces of the thermo-electric pile was exactly equal, which was indicated by the needle of the galvanometer standing precisely at zero. The gas for examination, after carefully drying it, was then admitted into the tube; under these circumstances, if the gas thus admitted were capable of absorbing even an exceedingly small portion of radiant heat, the equilibrium of the galvanometer was destroyed, and the needle was deflected to an extent varying with the amount of heat arrested during its passage through the gas.

Air	1	Carbonic anhydride	90
Oxygen	1	Nitrous oxide	355
Nitrogen	1	Sulphuretted hydrogen	390
Hydrogen	1	Marsh gas	403
Chlorine	39	Sulphurous anhydride	710
Hydrochloric acid	62	Olefiant gas	970
Carbonic oxide	90	Ammonia	1195

The absorptive power of many vapours for rays of obscure heat is still more remarkable; as will be seen by the following table, which shows a few of Tyndall's results at low pressures, compared with that of air at the normal pressure, taken as 1.

The absorbent action of the perfumes of many flowers for these obscure rays was also shown to be singularly high. A few drops of an essential oil placed in a tube, and exposed to a current of dry air, gave a scented atmosphere of which the absorptive power varied greatly; that of patchouli being 30, that of lavender 60, that of cassia 109, while that of aniseed was as high as 372; so that the perfume proceeding from a flower-bed absorbs a large proportion of the radiant heat of low refrangibility re-radiated from it.

Substance vaporized.	Pressure of Vapour.		
	2·5 mm. (0·1 inch.)	12·5 mm. (0·5 inch.)	25 mm. (1·0 inch.)
Bromine	about 1	...	6
Carbonic disulphide	15	47	62
Methyl iodide	35	147	242
Benzol	66	182	267
Chloroform	85	182	236
Wood spirit	109	390	590
Ethyl iodide	158	290	390
Amylene	182	535	823
Ether	300	710	870
Alcohol	325	622	
Formic ether	480	870	1075
Acetic ether	590	980	1195
Propionic ether	596	970	
Boracic ether*	620		

The experiments of Tyndall seemed to have completely established the fact that aqueous vapour has a powerful absorbent action upon heat of low refrangibility, although Magnus arrived at a different conclusion. (*Pogg. Annal.* 1867, cxxx. 207.)

* The results obtained by Tyndall on diluting boracic ether with air are so singular and anomalous, that there is reason to suspect some undiscovered source of error, boracic ether being a substance liable to decomposition even by a trace of moisture.

It must not be forgotten that hitherto Tyndall's experiments upon the various gases and vapours have been confined for the most part to radiant heat of low refrangibility. No doubt other and very different results will be furnished when heat of high refrangibility is made the subject of inquiry.

The radiation of heat by gases has also been clearly established by the experiments of Tyndall, and conformably with what we know of radiation and absorption in solids, he has proved that amongst gases the most powerful absorbents are likewise the best radiators.

(164) *Influence of Structure on Diathermancy.*—It by no means necessarily follows that a body which is transparent to light is also able to allow the passage of heat, and *vice versâ*; crystallized cupric sulphate, which permits the passage of blue light abundantly, arrests the rays of heat entirely. Again, the opaque black glass, used for the construction of polarizing mirrors, transmits a considerable portion of the thermic rays. Smoked rock salt and black mica also exhibit the same power.

Mechanical arrangement appears to have even more influence upon diathermancy than chemical composition. Common table salt is perfectly adiathermic. A solution of rock salt is scarcely superior to pure water in diathermancy, and a solution of alum is equally diathermic with a solution of rock salt. This is perfectly consistent with the effect which alteration of structure produces on the action of bodies on light. Common loaf-sugar is opaque and of dazzling whiteness, but pure sugar-candy (the same body only in larger crystals) is colourless and transparent: the most transparent glass, by pulverization, may be reduced to a white opaque powder.

As already mentioned, pure colourless rock salt is the only solid substance the diathermancy of which approaches perfection; and, according to the researches of Knoblauch, which have been confirmed by those of Stewart and others, even rock salt absorbs certain of the rays of heat, somewhat more freely than others; the rays thus absorbed are those of greatest wave length, or lowest refrangibility. All other bodies upon which Melloni made experiments, transmit a quantity of heat which varies greatly with the nature of the source, from a second cause, which has been termed *thermochrosis*, or calorific tint, which is analogous to a difference in colour for objects transparent to light; to this cause must be attributed the remarkable differences in the amount of absorption (161) according to the source from which the heat emanates. Before quitting this subject, it may be observed that B. Stewart

(*Proc. Roy. Soc.* 1860, x. 386) has shown that highly diathermic bodies are bad radiators, while adiathermic bodies are good radiators. He has proved that the radiation from a plate of rock salt goes on from a considerable depth below the surface: but the kind of heat which rock salt emits is the same which it absorbs, a thick plate of cold rock salt having been found to arrest at least three-fourths of the heat radiated from a thin plate of heated rock salt.

(165) *Refraction.*—Radiant heat, like light, is susceptible of refraction: a large convex lens, placed in the sun's rays, not only gives a focus of intense light, but, as is well known, constitutes a powerful burning-glass. Inflammable objects are easily ignited by this means, and the focus of heat is found to correspond nearly with that of the greatest light. Further, if a solar beam be subjected to the action of a prism of transparent rock salt, and the coloured spectrum so obtained be examined by means of a small but sensitive thermometer, it is found that the rays of heat, like those of light, possess unequal degrees of refrangibility; hence the rays of heat are not all accumulated in one spot, but are distributed over the entire spectrum. There are, in fact, differences in the rays of heat corresponding to those of colour in the rays of light. The greater portion of the rays of solar heat are even less refrangible than the red rays, for the maximum of temperature in the solar spectrum is found at a distance below the extreme red rays as great as the brightest yellow is above them. The length of the wave of these heat rays is consequently considerably greater than that of the red rays, and the frequency of undulation is proportionately less than that of the least refrangible luminous rays. As by the employment of different sources of light, spectra are obtained in which the intensity of the light varies in different parts according to the prevailing colour of the luminous rays,—the yellow light of common salt giving a spectrum most intense in the yellow rays, and the red light of strontic nitrate giving a spectrum in which the red rays possess the greatest intensity;—so in like manner, by varying the source of heat which is employed, the position of maximum temperature in the refracted beam is found to vary: the less intense the source of heat, the smaller is the refrangibility of the heat radiated. The flame of a naked lamp, for example, emits rays of heat of all degrees of refrangibility, its maximum of intensity being about the middle of the spectrum; from the ignited platinum, the maximum of heat falls nearer to the red; from copper still nearer still; and the heat radiated from a surface at

tains scarcely any of the more refrangible rays. Now it is obvious, that a mixed pencil of heat, if it falls upon a diathermic medium which absorbs certain of the rays of heat and not others, will be altered in a manner similar to that in which a ray of light is affected in traversing a coloured glass.

With a knowledge of these facts, there is no difficulty in understanding how it is that the sun's rays can traverse a plate of glass and experience but little absorption, and can be brought to a point by a convex lens, or by a glass concave mirror, either of which remains cool, while intense heat is developed at its focus; whereas, if the same lens or concave mirror be held opposite to a common fire, a bright spot of light will be obtained at the focus, but little or no heat; whilst the glass of which the lens or mirror is composed will become strongly heated. The rays which glass transmits most readily are those which abound in solar light, but these are precisely the rays which are least abundant in incandescent bodies. Advantage has long been taken of this fact by those who have occasion to inspect the progress of operations carried on in furnaces; they are able by the use of a glass screen to protect the face from the scorching rays which the glass absorbs, although it offers no impediment to the transmission of light.

This absorption of radiant heat by glass is easily demonstrated by placing a canister of hot water in the focus of one of the conjugate mirrors (fig. 131), and a thermoscope in the focus of the other: the air in the acting ball of this instrument ceases to expand the instant that a glass screen is interposed anywhere between the two mirrors, in which case the glass absorbs the rays, and becomes itself heated.

The foregoing observations show that in the analysis of radiant heat, prisms and lenses of glass should not be used, since they lead to results as incorrect as those which would be furnished by studying the phenomena of light by means of coloured prisms and lenses. Rock salt furnishes the only known material of which such apparatus can properly be constructed, and by its means, rays proceeding even from the human body may readily be concentrated and made to act upon a thermoscope.

(166) *Separation of Radiant Heat from Light.*—A consideration of the preceding facts led Melloni to expect that by a combination of screens which allow light of a given colour to pass, radiant heat may be arrested; and in fact he thus effected an apparent separation of light from heat. By transmitting the solar beam through a glass vessel filled with water, which arrests the refrangible rays, and then through a plate of a peculiar glass tinged by means of oxide of copper, which stops the

more refrangible rays, a greenish beam was obtained, which was concentrated by lenses, and furnished a greenish light of great intensity, but yet produced no perceptible heating action when it was allowed to fall upon the face of a sensitive thermoscope. A similar separation of light and heat seems to be effected in nature, in the light reflected by the moon. Melloni concentrated the rays of the moon by means of an excellent lens of a metre in diameter, and obtained a brilliant focus of light of 1 centimetre in diameter, the intensity of which consequently was nearly 10,000 times greater than that of the diffused light of the moon; upon directing this focus of light upon the face of a very sensitive thermo-multiplier, only an extremely feeble indication of heat was obtained.*—(Melloni, *Thermochrose*, Part I. note, 251.)

Lord Rosse has obtained evidence of the emission of heat from the moon by causing the image of the moon produced by

* Notwithstanding these results, Melloni maintained, during the latter years of his life, the identity of the agent that produces light and heat. Traces of heat, he says, are found in every luminous ray; he supposes that the rays of heat may be invisible, just as the chemical rays beyond the violet end of the spectrum are invisible, because the structure of the retina is not susceptible of undulations the frequency of which exceeds or falls short of a certain amount. No doubt there exists an average limit to the power of the retina to receive luminous impressions from solar radiations; the boundary between light and darkness being almost imperceptible. In certain individuals the retina is insensible to the extreme rays at the red end of the spectrum, which are plainly discerned by others. A parallel case occurs in the audibility of sounds: in some individuals the ear is unable to perceive notes in which, as in the chirp of a cricket, the vibrations exceed a certain number per second, though such sounds are distinctly audible to the majority of persons. Whether light can be obtained absolutely free from heat may still be doubtful, but there is no doubt of the existence of radiant heat of great intensity unaccompanied by light. According to Tyndall's observations upon his own eyes, the retina is quite insensitive to these obscure rays of heat, even when concentrated by a lens and thrown directly into the eye, though the focus of heat was sufficiently intense to kindle paper. It appears, therefore, from these experiments, that the intensity of the sensation of light which is experienced is by no means a measure of the intensity of the force by which the undulations which excite the sensation are produced, but that it is rather a measure of the exquisite sensitiveness of the retina to vibrations of certain degrees of frequency, and that above and below these points the retina becomes less and less sensitive, until at last a very much greater intensity of the force expended in producing the undulations fails to produce any sensation of light. Indeed, it is now assumed by those who adopt the undulatory theory of heat, that whenever light is absorbed, whatever be its source or intensity, it is converted into heat. Rigid experimental proof upon this point is, however, still wanting, though it is rendered probable, upon the principle of the conservation of energy, that the differences between the heating, the luminous, and the chemical rays are due to differences in the relative wave lengths; the rays of greatest wave length being the least refrangible.

his three-foot reflector to fall on the face of a thermo-electric pile which was connected with a Thomson's reflecting galvanometer. (*Proc. Roy. Soc.* 1869, xvii. 436.) Mr. Huggins has also detected the radiation of heat from the stars by placing a thermopile in the focus of a refractor of 8 inches aperture. (*Proc. Roy. Soc.* 1869, xvii. 309.)

In all experiments on radiated heat it has been observed that heat when once absorbed, whatever may have been its original source, acts in the same manner in producing expansion; and when radiated again it does not retain the peculiarities of the source from which it originated: the refrangibility of the re-radiated heat depends solely upon the temperature of the surface which emits it a second time; so that it is immaterial whether it were originally derived from the sun, from a lamp flame, from ignited platinum, or from non-luminous bodies; although it is well known that the refrangibility decreases with the temperature of the source from which it is derived. This alteration in the refrangibility of radiant heat corresponds with the discovery made by Stokes of a similar degradation of refrangibility in light (110). Heat of low refrangibility may, however, be converted into that of higher refrangibility: for example, a jet of mixed oxygen and hydrogen gases furnishes a heat nearly as intense as any which art can command, yet it does not emit rays which have the power of traversing glass in any considerable quantity, even though a lens be employed for their concentration. Upon introducing a cylinder of lime into the jet of the burning gases, though the temperature is not thus increased, the light becomes too bright for the unprotected eye to endure, and the thermic rays acquire the property of traversing glass, as is shown by their action upon a thermometer, the bulb of which is placed in the focus of the lens.

This observation has recently been fully confirmed by Tyndall, who, by the employment of a solution of iodine in carbonic disulphide, contained in a cell furnished with rock salt sides, has succeeded in absorbing the whole of the luminous rays, both of the sun and of the electric light. The rays of heat pass freely through the liquid, and by using a lens of rock salt he has condensed them to a focus in which he has thus kindled paper and other inflammable objects. By this means he has even succeeded in rendering a thin sheet of blackened platinum red hot; the rays employed are below the limit of the visible spectrum, and are less refrangible than the extreme red rays. In this manner the conversion of heat of low refrangibility into that of a refrangibility which is much higher has been amply demonstrated.

Tyndall states that carbonic disulphide saturated with iodine absorbs only about one-tenth of the heat rays emitted by the voltaic arc from charcoal points, though it retains nearly one-third of the heat of the solar spectrum, which abounds in heat rays of the higher degrees of refrangibility.

(167) By the employment of tourmalines, and by transmission through bundles of mica placed at suitable obliquities to the incident ray, it has been further proved that radiant heat is also susceptible of polarization; since the rays are reflected and transmitted alternately, according as the planes of reflection from the mica bundles coincide or cut each other at right angles. Knoblauch (*Pogg. Annal.* 1848, lxxiv. 9) has also obtained distinct evidence of the diffraction and interference of the rays of heat. The parallelism in the mechanical properties of radiant heat and of light is thus shown to be complete.

(167 *a*) *Repulsion caused by Radiation.*—In his determination of the atomic weight of thallium (*Phil. Trans.* 1873, 287), Mr. Crookes made the curious observation, that a heated body when weighed in a balance *in vacuo* appeared to weigh less than when it had the same temperature as the balance case. He has since followed out this phenomenon in a series of elaborate investigations (*Proc. Roy. Soc.* 1873, xxii. 37; *Phil. Trans.* 1874, 501; *Proc. Roy. Soc.* 1875, xxiii. 373; *Phil. Trans.* 1875, 519; *Proc. Roy. Soc.* 1876, xxiv. 276, 279, and 1876, xxv. 136, 304). The first experiments were made with a balance made of a straw with pith ball at each end, and placed within a glass tube from which the air could be removed. When the tube was filled with air, a repulsion was observed when heat was applied near one end of the balance; this was due to air currents, and on diminishing the pressure the repulsion became less. At the pressure of $7^{mm.}$ no effect was produced by the approach of a heated body; but on continuing the exhaustion, the repulsion became more powerful, and took place by the application of a lower temperature; a piece of ice caused attraction. A balance with brass balls was then tried, with a piece of platinum wire ignited by a battery placed within the tube; the effect in this case, when air was present, was to produce apparent attraction, caused by the currents rising from the hot platinum, and it was only when the pressure in the tube was reduced to less than half a millimetre that the ball was unaffected. On continuing the exhaustion, repulsion was found to take place by the approach of a heated body; a cold body, on the contrary, producing attraction. By employing a torsion balance, consisting of a horizontal rod carrying at its

ends different materials, and suspended at its centre by a single silk fibre, the repulsion was also shown, The different portions of the solar spectrum also acted in a similar manner. A still more delicate apparatus was afterwards made, in which the beam was supported by a very fine fibre of glass, and by means of a mirror attached to the beam, the slightest movement was readily perceived. Experiments seemed to indicate that the action was due to light, for when the heat rays were removed by absorbing media, the effect was still perceptible. On this principle, the *radiometer* was constructed—consisting of four arms delicately suspended on a pivot, and carrying at their extremities pieces of pith blackened on one side. When this was brought near a source of light, the black sides were repelled more powerfully than the white ones, and rapid rotation resulted. It was shown that a body heated to a low temperature produced no effect on the apparatus. Numerous explanations have been attempted to account for these phenomena, and it was not until it was found that the effect reached a maximum at a pressure of about 40 millionths of an atmosphere, and that at a lower pressure the repulsion was less, that it was proved that the action is due to residual gas. It appears, therefore, that radiation produces a small rise of temperature on the surface of the movable body, which causes a motion of the air molecules from the surface towards the surrounding case of the apparatus, resulting in a repulsion between the vanes of the radiometer and the enclosing vessel. This has been shown to be the case by Dr. Schuster (*Proc. Roy. Soc.* 1876, xxiv. 391), as well as by Mr. Crookes, who has determined the distances between two surfaces at which repulsion takes place at different pressures.

§ III. Specific heat—latent heat.

(168) *Specific Heat.*—It has been already stated (131) that the temperature of a body affords no indication of the actual quantity of heat which such a body contains. The thermometer does not even give the proportionate amount of heat which equal volumes of the same substance contain, if they be compared at different temperatures. It may, however, be made to furnish an estimate of the relative quantities of heat contained in two different masses, either of the same substance or of different substances. The mode in which this is effected we proceed now to illustrate.

Equal volumes of different kinds of matter, at the same temperature, contain very different quantities of heat. When

equal volumes of water, or of oil, or of any liquid, at different temperatures, are mixed with due precautions, they yield a mass the temperature of which is exactly the mean of the two. For instance, a litre of water at 32° F., added to a litre of water at 100°, gives two litres of water at 66°. But if two dissimilar liquids be used, the result is different. A litre of water at 32° mixed with a litre of mercury at 100°, gives a mixture the temperature of which is only 52°; but a litre of mercury at 32° mixed with a litre of water at 100°, gives a mixture having a temperature of 80°. Mercury is therefore often said to have less *capacity for heat* than water. It requires a smaller amount of heat to raise it a given number of degrees in temperature than is required to produce an equal elevation of temperature in the same volume of water. If equal weights of the two bodies be employed, instead of equal volumes, the difference is still more striking. A kilogramme of mercury at 20°, agitated with a kilogramme of water at 54°, gives a mixture the temperature of which is 53°. The water loses 1°, while the mercury gains 33°. The quantity of heat which would be required to raise any substance 1° C. in temperature, or more correctly, from 0° C. to 1° C., compared with the quantity of heat required to raise an equal weight of water through the same interval, is called its *specific heat*: therefore, taking the specific heat of water as 1, that of mercury will be 0·033.

(169) *Modes of Measuring Specific Heat.*—Three modes of determining the specific heat of a body have been employed. The best is the method of *mixtures* just described; another method consists in determining the *rate of cooling* of equal masses of the different bodies under similar circumstances; and the third consists in determining the amount of ice which a given mass of each body will melt when cooled from a fixed temperature, say 100° C., to the freezing point. This last method was employed by Lavoisier and Laplace; but though excellent in principle, the difficulties in practice render the results inaccurate.

If the body be in the solid form, the process of mixture may still be employed to ascertain the specific heat, by heating to the same degree of temperature, equal masses of the different solids which are to be compared, then immersing each in an equal volume of water, and observing the elevation of temperature produced in each case. Experiments conducted in this manner show that great differences in specific heats exist. Researches of this nature are necessarily attended with great difficulty, owing to the variety of sources of error, and the number of pre-

cautions required in order to insure accuracy. Full particulars upon these points are given in the papers of Dulong and Petit upon this subject (*Ann. Chim. Phys.* 1819 [2], x. 395), and of Regnault (*Ib.* 1840 [2], lxxiii. 5; 1841 [3], i. 129; 1843, ix. 322; 1849, xxvi. 261; 1856, xlvi. 257; and 1861, lxiii. 5).

In the *Phil. Trans.* for 1865 will be found an elaborate discussion by Kopp of the merits and defects of the various methods of determining specific heats. The following is the method which he has himself devised for determining speedily, and with considerable approach to accuracy, the specific heat of any substance either solid or liquid. If the material for trial be a liquid, it is introduced into a thin glass tube. The tube, with its contents, is heated by immersion in a mercury bath, which is maintained at a constant temperature, not exceeding 50° C., and then immediately plunged into a small calorimeter containing a known quantity of cold water, and the rise of temperature thus effected is accurately noted. If the calorific capacity of the tube without the liquid be first determined, and the amount so ascertained be deducted from the rise of temperature occasioned when the experiment has been repeated after the substance has been introduced into the tube, the specific heat of the substance under trial is easily calculated. If the material be solid, it is reduced to small fragments, or it is employed in the form of powder, and is placed in the glass tube with a known amount of a liquid in which it is not soluble, usually either water or coal naphtha. The calorific capacity of the tube with the naphtha is first ascertained, and then the experiment is repeated after the addition of the solid under trial.

The second mode of ascertaining the specific heat is founded on the different rates of cooling exhibited by equal masses of dissimilar composition; those which have the greatest specific heat cooling most slowly. The bodies are finely powdered, and introduced into an annular polished silver vessel, which is placed in a vacuous chamber coated internally with lamp-black, and surrounded by ice. By this arrangement the substances have virtually equal surfaces and equal radiating powers, and cannot be cooled by convection. The silver vessel, with a thermometer placed in its interior compartment, is heated to 30° or 40° C., and introduced into the chamber, from which the air is pumped as rapidly as possible; when the temperature indicated by the thermometer has fallen to 10° the time is noted, and again when the temperature has reached 5°, by determining the time occupied by each in cooling through this interval, and by comparing this with the time required by an equal quantity of water to cool

through the same thermometric interval, a series of numbers is obtained which represent approximately the specific heats of the bodies in question; making the time occupied by water in cooling, the unit of comparison, or 1. The differences in conductivity which varies greatly in the different bodies submitted to trial, is, however, a serious objection to the employment of this method for solids; for liquids it is less liable to error.

The following table gives a few of the results of Regnault upon specific heat, obtained by the process of mixture or immersion:—

Specific Heats of Equal Masses between 0° *C. and* 100° *C.*

Water	1·00000	Brass	0·09391
Oil of turpentin ...	0·42593	Silver	0·05701
Charcoal	0·24150	Tin	0·05623
Glass	0·19768	Mercury	0·03332
Iron	0·11379	Platinum	0·03243
Zinc	0·09555	Gold	0·03244
Copper	0·09515	Lead	0·03140

(169 *a*) *Causes of Alteration of Specific Heat.*—Any circumstance which alters the relative distances between the particles of which a body is composed, at the same time alters its specific heat. Mechanical compression sufficient to produce a permanent alteration in density is attended by a corresponding decrease in specific heat:—For instance, the specific heat of a piece of soft, well-annealed copper was found to be from 0·09501 to 0·09455; the same copper, after hammering, had a specific heat of from 0·0936 to 0·0933; on being again thoroughly annealed, so as to recover its former density, its specific heat was from 0·09493 to 0·09479, or almost exactly the same as at first. Again, in dimorphous bodies (86) the densest form has in some cases been found to possess the lowest specific heat. Regnault (*Ann. Chim. Phys.* 1841 [3], i. 204) found that diamond, for example, has a specific heat of 0·1468; whilst graphite has a specific heat of 0·2018, or one-third higher; and the specific heat of charcoal is still higher, or 0·2415. Kopp, however, considers that this rule is not general; the specific heats of calc spar and aragonite, iron pyrites and marcasite, rutile and brookite being scarcely different. It has also been thought that to this diminution of specific heat by compression may be partially due the heating of cold metallic bars observed during the operation of rolling: they become denser, and consequently have less capacity for heat. It is, however, more probable that this is simply a case of the conversion of sensible motion into the molecular motion which produces heat, similar to that which attends friction or percussion.

The sudden compression of aeriform bodies is likewise attended with the evolution of a very large amount of heat, which may even rise high enough to ignite tinder and other inflammable substances. On rarefying air the opposite effects are observed. One evidence of this fact is afforded by the mist which is formed within a glass receiver while it is undergoing exhaustion. On first working the pistons of the air-pump, the sudden expansion deprives the moisture which all air contains, of part of the heat necessary for its existence in the gaseous form, and it condenses in minute drops, which speedily evaporate again as the equilibrium of temperature is restored. If compressed air be allowed to expand suddenly, by escaping into the atmosphere, a similar phenomenon is produced; a demand for the heat which the air had lost in compression suddenly arises, and moisture is deposited as before.

It was formerly supposed that this absorption of heat attending the expansion of aeriform bodies was due to an alteration in their specific heat, but the careful and elaborate experiments of Regnault have proved that this is not the case, and the absorption of heat under these circumstances affords a strong argument in favour of the mechanical theory of heat.*

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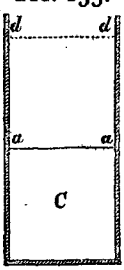
* It may be worth while to examine the conditions under which this diminution of temperature takes place somewhat more fully. Suppose two equal volumes of air at 0° C. be exposed to the action of a gradually increasing temperature until each is raised to a temperature of 273° C. If one of these volumes of air be allowed to expand unchecked, its pressure will remain unaltered, but its volume will be doubled; whilst if the other is confined within fixed limits, its volume will be unaltered, but its pressure will be doubled. The quantity of heat absorbed to produce the observed rise of temperature will, however, be very different in the two experiments. In the case where the air is allowed to expand, the heat required will be greater than where the volume of the air continues the same—in the ratio of 1413 to 1000; or the quantity of heat consumed when the air is not allowed to expand will be about $\frac{2}{7}$ less than when the expansion occurs under the usual atmospheric pressure. Let *C*, fig. 133, be an open rectangular vessel, the base of which is one square metre in area. If *a a* represent the surface of a cubic metre of air contained within it at a temperature of 0° C., *d d* will represent the surface of the same cubic metre of air which has been raised to 273° C. The quantity of air which originally filled but one cubic metre will now occupy the space of two cubic metres; consequently it must have lifted the superincumbent column of atmospheric air, resting on the surface *d d*, through a height of one metre; but the weight of that superincumbent column of air, calculated at 1·03329 kilos. per square centimetre is 10,332·9 kilos. Now, a cubic metre of air at 0° C. is 1·293187 kilogr., and the specific heat of air was found by Regnault to be a little less than one-fourth of that of water, or 0·2375, so that

FIG. 133.



The absorption of heat by air when it undergoes rarefaction, will enable us to understand the general distribution of temperature in any vertical column of the atmosphere of our globe. If the atmosphere, without being altered in quantity, could be reduced to a stratum of uniform density throughout, with a uniform temperature of 30° C., it would extend to a height of about 5·4 miles, or 8690 metres. Now, suppose that this air, throughout the entire thickness of the stratum, suddenly expanded to the extent due to its elasticity; the temperature would immediately fall in every part of the column (except at its base, where it would remain stationary), in consequence of the alteration in density; at 5000 metres it would be about 0° C., and at 10,000 metres it would be about − 22° C. It may be shown, indeed, that a column of air in equilibrium is at uniform temperature, but this is a condition which cannot occur in the atmosphere of the earth. Air allowing heat to pass through it without raising its temperature, the sun's rays produce very little effect on the atmosphere until they strike the surface of the earth, this being heated warms the air in contact with it, expanding it, and producing a rise of warm air. On rising, the air is submitted to reduced pressure, and the resulting expansion

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the quantity of heat required to raise 1·293187 kilogr. of air 273° will raise only 0·307132 kilogr. of water through 273° C. Now, 0·307132 kilogr. of water raised to 273° C. would be equal to 83·847 kilos. raised only 1°. Thus the heat required to double the volume of a cubic metre of air, and consequently to lift 10,332·9 kilos., would heat 83·847 kilos. of water 1° C., or would be 83,847 units of heat.

Suppose, in the next place, that the cubic metre of air, instead of being allowed to expand freely, be confined when heated, so that its volume shall remain constant; the quantity of heat required under these circumstances will be less than when it was allowed to expand freely in the ratio of 1413 to 1000, so that the quantity of water which would be heated 1° by this amount is easily seen to be only equal to 59·3397 kilos.; for 1413 : 1000 :: 83·847 : 59·3397.

Now, on deducting 59·3397 from 83·847, the difference, 24·5073, represents the number of kilogr. of water which would be raised 1° C. by the excess of heat imparted to the air when allowed to expand, in our imaginary experiment; but this excess, as already explained, has been engaged in lifting a column of air of 10,332·9 kilogr. weight through a height of one metre. If now we divide 10,332 9 kilos. by 24·5073, we obtain a number 421·625 kilos., and hence it appears that an expenditure of heat sufficient to raise one kilogr. of water 1° C. is competent to raise 421·625 kilos. one metre; or we are by this means brought to nearly the same result as that deduced by Joule from his experiments. The reasoning employed above is that used by Mayer in his paper on the mechanical nature of heat. The numbers, however, have been supplied by subsequent experiments. We assume, however, in this experiment, that the interior energy of the air remains the same. (See Tyndall: *Heat as a Mode of Motion*, 4th edit. p. 68, *et seq.*)

lowers its temperature. That this does take place on a large scale is well shown in the formation of cumulus cloud during a calm day after a cloudless night; the sun heating the surface of the ground evaporates the dew, and the warm and moist air rises. At a certain distance above the earth's surface the temperature of the air is lowered by expansion to the dew point, and the aqueous vapour is condensed in the form of a cloud with a nearly horizontal lower surface and a rounded top. The action of wind also causes an elevation of portions of the air which are thus cooled. If no circulation took place in the air, the temperature of the lower strata would be very much raised above that of the upper in consequence of their contact with the earth; and the actual temperatures of the different layers are probably intermediate between those which would be produced under this condition and those caused by the sudden ex-expansion of the air, as described above. A progressive diminution of the temperature is experienced, as the altitude of the observer above the surface of the earth increases; and this depression of temperature is such, that even in tropical climates, the summits of lofty mountains are always crowned with snow. At the equator the snow line occurs at an altitude of about 5000 metres, but in England the line of perpetual snow occurs at about 2000 metres, since the limit of perpetual snow gradually descends (subject, however, to irregularities, from local causes) towards the level of the sea, according as the place of observation approaches towards either pole. A blast of cold air, therefore, in descending from a lofty height would have its temperature elevated by the mere condensation which it experiences as it approaches the surface of the globe, without any supply of heat from extraneous sources; and the danger arising from its chilling influences would be thus simply and effectually averted. Observations have shown that the average depression of temperature in ascending from the sea level amounts to 1° F. for every 300 feet, or 1° C. for every 165 metres. The observations made by Glaisher in his balloon ascents have, however, shown that in our own latitude this regularity of progression is liable to considerable disturbance from currents which are variable in direction and in force. The following table is given by Daniell (*Meteorology*, 1845, i. 41) as an approximate estimate of the distribution of heat in the atmosphere due to this cause, supposing, as indicated in the second column, that the initial temperature of 80° is that of the surface of the earth near the equator, and that the initial temperature of 0° F. indicated in

the third column is that towards the poles: but from what has been stated above, the vertical distribution of temperature in the air is much more complex than was formerly supposed.

Decrease of Temperature in the Atmosphere from Elevation.

Altitude in feet.	Temperature ° F.	Temperature ° F.
0	80°	0°
5000	64·4	−18·5
10000	48·4	−37·8
15000	31·4	−58·8
20000	12·8	−82·1
25000	−7·6	−109·1
30000	−30·7	−140·3

In proportion as the temperature of a substance rises, its specific heat gradually increases: owing, probably, to the increase in the volume of the body with the rise of temperature, and to the augmentation of the space between the molecules of the heated substance. This increase in the specific heat with the rise of temperature may be seen by examining the following table compiled from the experiments of Dulong and Petit:—

Rise of Specific Heat with Rise of Temperature.

Substance used.	From 32° to 212° F. or 0° C. to 100° C.	From 32° to 572° F. or 0° C. to 300° C.
Mercury	0·0330	0·0350
Platinum	0·0335	0·0355
Antimony	0·0507	0·0549
Silver	0·0557	0·0611
Zinc	0·0927	0·1015
Copper	0·0949	0·1013
Iron	0·1098	0·1218
Glass	0·1770	0·1900

(170) *Variation of Specific Heat with Change of Physical State.*—A body in the liquid state has a higher specific heat than the same substance when it is in the solid form. It is lower in the gaseous than in the liquid condition. This is remarkably shown in the case of water, in which the specific heat is double that of ice, and also more than double that of steam. Contrasting together the specific heats, as obtained for the following solids by Regnault, with the numbers obtained by Person (*Ann. Chim. Phys.* 1847 [3], xxi. 295, and 1848, xxiv. 129) for the same bodies when liquefied, the amount of this difference will be seen to be liable to great variation:—

Specific Heat of the same Substance, both in the Solid and in the Liquid State.

Substance.	Solid.		Liquid.	
	Sp. Heat.	Temperature °C.	Sp. Heat.	Temperature °C.
		between		between
Ice	0·5040	−30° and 0°	1·0000	0° and 20°
Sodic Nitrate	0·2782	0° and 100°	0·4130	320° and 430°
Potassic Nitrate	0·2387	0° and 100°	0·3318	350° and 435°
Sulphur	0·2026	0° and 100°	0·2340	120° and 150°
Phosphorus	0·1788	−21° and 7°	0·2045	50° and 100°
Bromine	0·0843	−78° and −20°	0·1060	−73° and 10°
Tin	0·0562	0° and 100°	0·0637	250° and 350°
Iodine	0·0541	0° and 100°	0·1082	not stated
Lead	0·0314	0° and 100°	0·0402	350° and 450°
Bismuth	0·0308	0° and 100°	0·0363	280° and 380°
Mercury	0·0319		0·0333	10° and 100°

Of all solids and liquids water is that which possesses the highest specific heat. This circumstance contributes in no small degree towards moderating the rapidity of transitions from heat to cold, or from cold to heat, owing to the large quantity of heat which the ocean absorbs or emits in accommodating itself to the variations of external temperature. Mercury, on the other hand, has a very low specific heat, which much enhances its sensibility to changes of temperature, and increases its fitness for thermometric purposes.

Specific Heat of Gases and Vapours.

Gas or Vapour.	Equal.		Gas or Vapour.	Equal	
	Vols.	Weights.		Vols.	Weights.
Air	0·2375	0·2375	Sulphurous Anhydride	0·341	0·154
Oxygen	0·2405	0·2175	Hydrochloric Acid	0·2375	0·1845
Nitrogen	0·2368	0·2438	Sulphuretted Hydrogen	0·2857	0·2432
Hydrogen	0·2359	3·4090	Water	0·2996	0·4805
Chlorine	0·2976	0·1210	Alcohol	0·7224	0·4534
Bromine	0·3076	0·0555	Wood Spirit	0·5076	0·4580
Nitrous Oxide	0·3447	0·2262	Ether	1·2294	0·4797
Nitric Oxide	0·2406	0·2317	Ethyl Chloride	0·6096	0·2738
Carbonic Oxide	0·2370	0·2450	Ethyl Bromide	0·7158	0·1896
Carbonic Anhydride	0·3307	0·2163	Diethyl Sulphide	1·2493	0·4008
Carbonic Disulphide	0·4133	0·1570	Ethyl Cyanide	0·8119	0·4262
Ammonia	0·2996	0·5084	Chloroform	0·6486	0·1567
Marsh Gas	0·3277	0·5929	Dutch Liquid	0·7862	0·2293
Olefiant Gas	0·4106	0·4040	Acetic Ether	1·2216	0·4008
Arsenious Chloride	0·7053	0·1122	Benzol	1·0141	0·3754
Silicic Chloride	0·7784	0·1322	Acetone	0·8286	0·4125
Titanic Chloride	0·8578	0·1290	Oil of Turpentin	2·3839	0·5061
Stannic Chloride	0·8456	0·0939	Phosphorous Chloride	0·6415	0·1347

(171) *Specific Heat of Gases and Vapours.*—The determination of the specific heats of gases and vapours is attended with unusual difficulties; and the earlier researches on the subject, though conducted by many philosophers distinguished for experimental skill, gave discordant and unsatisfactory results.

The subject has been submitted to a very elaborate and rigorous investigation by Regnault, who, taking the specific heat of water as the unit of comparison, finds that of air to be $=0{\cdot}2375$, and he gives the foregoing numbers as representing the specific heat of the various gases and vapours upon which he made his experiments.

As the result of a numerous and elaborate series of experiments, Regnault concludes, contrary to the statement of Delaroche and Bérard, that the specific heat of air does not increase with rise of temperature, at any rate between the temperatures of -30° and 200° C. The same result holds good for gases which, like hydrogen, are not readily liquefiable. Condensible gases like carbonic anhydride exhibit a variation which, on the contrary, is quite perceptible: thus, the specific heat of carbonic anhydride—

Between	-30° and 10° C.	was found	$=0{\cdot}18427$.
„	$+10^\circ$ and 100°	„	$=0{\cdot}20246$.
„	$+10^\circ$ and 210°	„	$=0{\cdot}21692$.

Or the specific heat of carbonic anhydride is as follows:—

At	0° C.	$=$ $0{\cdot}1870$.
„	100°	$=$ $0{\cdot}2145$.
„	200°	$=$ $0{\cdot}2396$.

A similar variation, though probably to a still greater extent, occurs with vapours generally.

Another remarkable experimental result obtained by Regnault, indicates that for pressures ranging between 1 and 12 atmospheres, the specific heat of *equal weights* of a non-condensible gas, such as atmospheric air or hydrogen, is uniformly the same, and is independent of the density; consequently, that the specific heat of a given *volume* of a gas increases directly as its density is increased.

The specific heats of the simple gases for equal volume, are nearly the same in the case of the incondensible gases—oxygen, nitrogen, and hydrogen—and appear to follow the law of Dulong and Petit (172); but for condensible gases and vapours, such as chlorine and bromine, it is far from being true. Compound gases which are formed without undergoing condensation, such as hydrochloric acid and nitric oxide, also obey the law of Dulong

and Petit. When a body can be obtained in the solid, liquid, and gaseous states, it is found to have the highest specific heat when in the liquid form, and much less in the aëriform state.

Specific Heats of Liquids and Vapours compared.

Liquid.	Formula.	Liquid.		Gaseous.	
		Sp. heat.	Temp. °C.	Sp. heat.	Temp. °C.
Water	H_2O	1·0000	between 11° and 100°	0·4805	between 128° and 220°
Bromine	Br_2	0·1060 0·1129	−29° and 11° 13° and 58°	0·0555	83° and 228°
Alcohol	C_2H_6O	0·505 0·7694	At −20° At 80°	0·4534	107° and 220°
Ether	$C_4H_{10}O$	0·5113 0·5467	At −30° At 30°	0·4797	70° and 223°
Carbonic Disulphide	CS_2	0·2303 0·2401	At −30° At 30°	0·1570	73° and 192°
Wood Spirit	CH_4O	0·6700	0° and 20°	0·4580	101° and 223°
Acetone	C_3H_6O	0·4824 0·5302	At −30° At 30°	0·4125	129° and 233°
Diethyl Sulphide ...	$C_4H_{10}S$	0·4785	20° and 70°	0·4008	120° and 223°
Ethyl Chloride ...	C_2H_5Cl	0·4275	−27° and 4°	0·2738	19° and 172°
Ethyl Bromide ...	C_2H_5Br	0·2160	0° and 20°	0·1896	78° and 196°
Ethyl Cyanide ...	C_2H_5Cy	0·4325 0·5847 0·7369	At −30° At 30° At 90°	0·4262	114° and 221°
Ethyl Acetate ...	$C_2H_5C_2H_3O_2$	0·4960 0·5588	At −30° At 30°	0·4008	115° and 219°
Chloroform	$CHCl_3$	0·2293 0·2354	At −30° At 30°	0·1567	117° and 228°
Dutch Liquid	$C_2H_4Cl_2$	0·2790 0·3054	At −30° At 30°	0·2293	111° and 221°
Benzol	C_6H_6	0·4360	0° and 71°	0·3754	116° and 218°

In determining the specific heats of gases and vapours, after a trial of various methods, Regnault ultimately adopted a modification of that employed by Delaroche and Bérard:—The gas under trial was first condensed into a strong receiver, and then by means of apparatus especially contrived for the purpose, a known quantity of this gas was allowed to escape at a perfectly constant rate, into a long spiral tube plunged into a vessel of hot oil, which was maintained at a fixed temperature; the gas was in this way during its passage through the spiral, raised to a known temperature, equal to that of the oil in the bath; the heated gas was then transmitted through a metallic vessel, surrounded by a known quantity of water; finally, the gas was allowed to escape into the atmosphere, care being taken that no sensible difference in temperature existed between the issuing gas and the water of the calorimeter. In this way Regnault ascertained the rise of temperature experienced by a known quantity of water, when a given

quantity of each gas, after it had been raised to a certain known temperature, was cooled down by it to a certain other known temperature. When the specific heat of equal *masses* of the different gases was once known, it was easy to calculate that for equal *volumes*, by simply multiplying the numbers for equal weights by those representing the densities of each gas or vapour. For the details of this delicate inquiry, the reader is referred to the second volume of Regnault's great work, *Relations des Expériences pour déterminer les Lois et les Données Physiques nécessaires au Calcul des Machines à Feu*, 1862, 41—333.

The foregoing table, compiled from Regnault's experiments, shows how greatly the specific heat of the same liquid varies with the temperature, whilst in gases no such variation takes place. It also shows that the specific heat of a body in the gaseous state is always less than that of the same substance in the liquid state.

(172) *Relation of Specific Heat to Atomic Weight.*—An interesting relation has been traced between the specific heats of bodies and their combining quantities. It has already been stated (168) that the amount of heat required to raise equal masses of different substances 1° in temperature varies for each species of matter, but is always constant for the same body when it is placed under like circumstances.

By comparing together quantities of the various elementary substances in the ratio of their combining proportions, and ascertaining the amount of heat which each requires to raise it through equal intervals of temperature, Dulong and Petit made the important observation that the quantities of heat absorbed bear a very simple numerical relation to each other. In a large number of instances, the amounts of heat thus absorbed, allowing for unavoidable errors of experiment, are identical; and it was further observed, that the exceptional cases nearly always exhibit some simple multiple relation to this number. In other words, *the specific heat of an elementary body is inversely as its combining proportion:* consequently, the product of the specific heat of an element into its combining proportion gives, subject to slight variations due to errors of experiment, either a constant number, or some multiple of that number.

The law thus announced by Dulong and Petit has been confirmed by the subsequent researches of Regnault upon specific heat (*Ann. Chim. Phys.* 1840 [2], lxxiii. 61; 1841 [3], i. 129; 1843, ix. 322; 1849, xxvi. 261; 1853, xxxviii. 129; 1856, xlvi. 257; and 1861, lxiii. 5). Regnault determined the specific heats of a great variety of bodies, both simple and compound. He

designated the product obtained by multiplying the specific heat of a body by its atomic weight, as the *atomic heat* of the body.

In 21 of the simple bodies which he examined, most of which were in a state of chemical purity, he found the atomic heat to range between 3·31 and 2·93, with a mean of 3·13. The elements comprised in this class are the following—viz., aluminium, cadmium, cobalt, copper, iridium, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, osmium, platinum, rhodium, selenium, sulphur, tellurium, tin, tungsten, and zinc. Experiments are at present wanting upon barium, strontium, calcium, glucinum, thorinum, cerium, didymium, lanthanum, vanadium, uranium, and ruthenium; although from analogy there is reason to believe that they belong to this group of elements as regards their specific heat. No direct experiments upon the specific heat of oxygen in a form comparable with the solid elements have yet been made.

When the *equivalent* number formerly regarded as the atomic weight was employed as the multiplier of the specific heat, it was found that a second smaller class of elements exists which have an atomic heat double that of the elements contained in the foregoing list. This class comprises gold, silver, thallium, bismuth, antimony, arsenic, phosphorus, bromine, and iodine, as well as lithium, potassium, and sodium. From their chemical analogies, there can be little doubt that in this list should also be included chlorine, cæsium, and rubidium, although as yet the necessary experiments are wanting to decide the point. The bodies of this class gave for their atomic heat numbers ranging between 5·85 and 6·87, with a mean of 6·42; Regnault therefore proposed to divide by two the numbers usually given as the atomic weights of the elements in the second list. It was found more convenient to double the atomic weights of the first series, by which means the identity of the ratio was preserved equally well. There are chemical reasons which fully justified this alteration, startling as it at first appeared. The *combining proportion* of an element, it must be remembered, is not affected by this change of the number which, for various reasons, is selected as the *atomic weight*, and which in some cases coincides with the combining proportion, while in others it is a multiple of it.

Dulong and Petit's law may therefore be stated thus. If, instead of taking equal weights, we compare together quantities of the elementary bodies in the proportion of their atomic weights, these quantities will be found to require equal amounts of heat

to raise them through an equal number of degrees of temperature. There are, however, still some marked exceptions to the law, particularly among the non-metallic elements.

Specific and Atomic Heats of the Elements.

Elements.	Specific Heat of Equal Masses.	Equivalent.	Specific Heat × Equivalent.	Atomic Weight.	Specific Heat × At. Weight.	Masses containing equal quantities of Heat.
Diamond	0·1469	6	0·8814	48?	7·0512	44·83
Graphite	0·2018	,,	1·2108	33?	6·6594	32·63
Wood Charcoal	0·2415	,,	1·4490			27·27
Silicon, fused	0·1750	14	2·450	35?	6·125	37·63
,, crystallized	0·1767					37·27
Boron, crystallized	0·250	11	2·75			26·34
Sulphur (native)	0·20259	16	3·2414	32	5·6832	32·51
Selenium	0·08370	39·75	3·3272	79·5	6·6544	78·68
Tellurium	0·04737	64·5	3·0553	129	6·1107	139·02
Magnesium	0·2499	12	2·9988	24	5·9976	26·35
Zinc	0·09555	32·5	3·1054	65	6·2108	68·92
Cadmium	0·05669	56	3·1746	112	6·3492	116·17
Aluminium	0·2143	13·75	2·9480	27·5	5·8960	30·73
Iron	0·11379	28	3·1861	56	6·3722	57·87
Nickel	0·1073	29·5	3·1653	59	6·3306	61·38
Cobalt	0·1108	29·5	3·2686	59	6·5372	59·44
Manganese	0·1217	27·5	3·3467	55	6·6934	54·11
Tin	0·05623	59	3·3176	118	6·6352	117·12
Tungsten	0·03342	92	3·0746	184	6·1492	197·06
Molybdenum	0·07218	48	3·4646	96	6·9292	91·24
Copper	0·09515	31·7	3·0162	63·4	6·0325	69·21
Lead	0·03140	103·5	3·2499	207	6·4998	209·73
Mercury, solid	0·03192	100	3·1920	200	6·3840	206·32
,, liquid	0·03332	100	3·3320	200	6·6640	
Platinum	0·03243	98·55	3·1960	197·1	6·3920	203·07
Palladium	0·05927	53·25	3·1561	106·5	6·3123	111·11
Rhodium	0·05408	52·2	2·8292	104·3	5·6405	121·78
Osmium	0·03063	99·5	3·0477	199	6·0954	215·00
Iridium	0·0363	99	3·5937	198	7·1874	181·42
Iodine	0·05412			127	6·8732	121·69
Bromine, solid	0·08432			80	6·7456	78·10
,, liquid	0·10600			80	8·4800	
Potassium	0·16956			39·1	6·6298	38·84
Sodium	0·29340			23	6·7482	22·45
Lithium	0·9408			7	6·5856	7·00
Phosphorus	0·18870			31	5·8497	34·90
Arsenic	0·08140			75	6·1050	80·90
Antimony	0·05077			122	6·1939	129·71
Bismuth	0·03084			210	6·4764	213·54
Thallium	0·03255			203·6	6·6272	202·32
Silver	0·05701			108	6·1570	115·52
Gold	0·03244			196·6	6·3777	203·01
Uranium	0·0619			120	7·4280	106·39
Indium	0·057			113·4	6·4637	115·54
Glucinum or Beryllium	0·6424			9·3	5·9743	10·252

The above table includes some of the principal results derived from Regnault's experiments on a large number of elementary

bodies. He found, as has been already stated, that the same element has a different specific heat if examined in a different state of aggregation. Bodies when in the liquid form have a higher specific heat than when in the solid state, as is seen on comparing the numbers for bromine and mercury in the two conditions.

An extended table, embracing the principal results obtained on the specific heat of solids, both simple and compound, by various observers, is given by Kopp (*Phil. Trans.* 1865, 168).

Amongst the non-metallic elements there are, as above stated, certain striking exceptions to the law of Dulong and Petit. Carbon, for instance, as diamond, taking its atomic weight as 12, has an atomic heat of only 1·7616; the atomic heat of crystallized boron is 2·725; that of fused silicon 4·9; that of octohedral sulphur 5·6832; and that of phosphorus 5·8497.*

Dewar (*Phil. Mag.* 1872 [4], xliv. 461) found the specific heat of gas carbon between 1040° and 20° to be 0·32; and between 2000° and 20° it was ·42, from which he estimated the true specific heat at 2000° to be at least ·5.

Some experiments have recently been made by Weber (*Phil. Mag.* 1875 [4], xlix. 161, 276) which show that the specific heats of carbon, silicon, and boron increase rapidly as the temperature rises, and that these elements are not exceptions to the law of Dulong and Petit, when their specific heat is determined at sufficiently high temperatures.

	Specific Heat of Equal Masses.	Specific Heat × Atomic Weight.	Masses containing same quantity of Heat as 7 parts of Lithium.
Carbon at and above 600° ...	0·46	5·52	14·316
Silicon (crystallized) at and above 200°	0·205	5·76	32·12
Boron (crystallized)	0·5 about.	5·5 about.	13·172 about.

The relation between the atomic weights and specific heats is well illustrated by the last column in the table, containing the

* Kopp suggested that these exceptional cases may have their origin in the circumstance that we have as yet no absolute proof that the bodies now regarded as elements are really the simplest forms of matter; and that the metals and all the so-called elements which have the higher atomic heat 6·4 may possibly be compounds; whilst the diamond, which has the lowest atomic heat, 1·8, may be really the only elementary substance known to us—the bodies with intermediate atomic heats being truly compounds more complex than carbon, but less so than the metals.

weights of the different solid elements, which, under the same conditions, exhibit the same specific heat as seven parts by weight of lithium. In most cases these numbers are the same as the atomic weights, allowance being made for errors of experiment.

(173) *Molecular Heats of Compound Bodies.*—The alloys, according to Regnault's experiments, yield a specific heat which is exactly the mean of that of their components; hence their specific heat is equal to the sum of that of their components; and Woestyn (*Ann. Chim. Phys.* 1848 [3], xxiii. 295), has shown that for the sulphides and iodides, within certain limits of error, the molecular heat may be calculated from the sum of the atomic heats of their constituents; and Garnier maintains that this is true for all bodies. The same conclusion has also been arrived at by Kopp.

On comparing together equivalent quantities of isomorphous compounds possessed of a similar chemical composition, Neumann (*Pogg. Annal.* 1831, xxiii. 37) found that they likewise possess equal molecular heats. The differences from the mean are in some cases considerable, but they are of the same order as those already observed to occur in the simple bodies. The mean molecular heat of the isomorphous carbonates, such, for example, as the carbonates of calcium, barium, iron, lead, zinc, strontium, and the double carbonate of calcium and magnesium, is 20·99, varying between 20·08 and 21·73. In like manner the sulphates of barium, calcium, strontium, and lead yield a mean molecular heat of 25·57.

Regnault, from an extensive series of experiments on a great variety of compound bodies, arrived at the conclusion that, "in all compound bodies of the same atomic composition, and of similar chemical constitution, the specific heats are inversely as the atomic weights." The product obtained by multiplying the specific heat into the molecular weight in any one class of compounds may, however, differ greatly from the product of the corresponding numbers in any other class, the numbers furnished by the different classes not being connected by any very simple ratio. These facts will be rendered obvious by an examination of the subjoined summary of Regnault's results (*Ann. Chim. Phys.* 1841 [3], i. 172).

In the last column of the table are given the quotients obtained by dividing the molecular heat in the fourth column by the number of atoms entering into the composition of the compound.

These quotients are not uniform in amount, as would be the case if the atomic heats of all the elements were alike, and if the molecular heat of a compound were represented by the sum of the atomic heats of its constituent elements; but it may be easily seen that the number in the different members of the same class of compounds is nearly alike.

For example, assuming that the molecule of the chlorides of the alkaline metals is represented by the formula MCl (a diatomic formula), the molecular heat of this class, 12·88, divided by 2, is 6·44, which agrees very well with the ordinary number for the atomic heat of the elements. Again, if the molecule of the chlorides of the metals of the alkaline earths, and most of the strongly basic metals, iron, cobalt, zinc, nickel, &c., be represented by the formula $N''Cl_2$ (a triatomic formula), the molecular heat 18·65, divided by 3, gives 6·22 as the result, again agreeing with the ordinary numbers for the atomic heat of the elements. Similar remarks are applicable in the case of the bromides and the iodides of these two classes of metallic elements, as will be obvious on inspecting the table opposite.

This correspondence between these two sets of chlorides, bromides, and iodides, however, disappears, if it be supposed, as till recently was generally admitted, that the chlorides, bromides, and iodides are all diatomic. If the chlorides of the second class represented in the table as consisting each of 3 atoms—such as chlorides of calcium, barium, magnesium, &c., be supposed to be formed upon the type MCl, or to contain two atoms only in their molecules—their molecular heat will be 9·32, and dividing by 2, the number will be 4·66.* The general conclusion deducible from these experiments is that, whilst the equivalents of the halogens and of the alkaline metals, including also thallium and silver, are truly their atomic weights, the equivalents of the

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* This may, perhaps, be rendered more clear by an example:—The specific heat of baric chloride is, 0·08957; if it be represented by the formula BaCl, with an atomic weight 104·0, its atomic heat will be $0{\cdot}08957 \times 104 = 9{\cdot}315$; whereas if it be represented as $Ba''Cl_2$, with an atomic weight 208, its atomic heat will be just double, or 18·63. In the first case, the molecule of the salt is supposed to be diatomic, or to contain 2 atoms of its constituents; in the second it is represented as triatomic, or as containing 3 atoms. The quotient obtained by dividing the atomic heat by the number of atoms in the molecule will of course be different in the two cases:—

$$\text{for } \frac{9{\cdot}315}{2} = 4{\cdot}657; \text{ and } \frac{18{\cdot}63}{3} = 6{\cdot}21.$$

majority of the remaining elements represent but half their atomic weights.

Molecular Heat of Compounds.

Class of Compounds.	General Formula.	No. of examples.	Sp. Heat × Mol. Weight.	Mol. Heat. No. of Atoms.
Protoxides, 1st Class ZnO ...	N″O*	2	9·93	4·97
„ 2nd Class, PbO	N″O	7	11·50	5·75
Sesquioxides	R'''_2O_3	8	26·83	5·37
Dioxides	$X^{iv}O_2$	3	14·01	4·67
Trioxides	$Y^{vi}O_3$	2	18·58	4·64
Sulphides	M_2S	2	18·88	6·29
Sulphides	M″S	7	11·93	5·96
Sesquisulphides	R'''_2S_3	2	29·77	5·95
Disulphides...	$X^{iv}S_2$	2	20·72	6·91
Chlorides	MCl	5	12·88	6·44
Dichlorides	N″Cl_2	8	18·65	6·22
Trichlorides...	R‴Cl_3	2	30·36	7·59
Tetrachlorides	$X^{iv}Cl_4$	2	37·57	7·51
Bromides...	MBr	3	13·88	6·94
Dibromides	N″Br_2	1	19·55	6·52
Iodides	MI	5	13·42	6·71
Diniodides	N″I_2	2	19·36	6·45
Fluorides	N″F_2	1	16·76	5·58
Nitrates	MNO_3	3	24·079	4·82
Nitrates	N″2 NO_3	1	39·74	4·42
Chlorates	$MClO_3$	1	25·69	5·14
Sulphates	M_2SO_4	2	32·97	4·71
Sulphates	N″SO_4	5	26·44	4·41
Chromates	M_2CrO_4	1	36·03	5·15
Anhydro Chromates	$M_2Cr_2O_7$	1	55·90	5·08
Carbonates	M_2CO_3	2	29·40	4·90
Carbonates	N″CO_3	8	21·42	4·28
Phosphates...	N″$_3$ 2 PO_4	1	64·73	4·98
Metaphosphates	N″ 2 PO_3	1	39·45	4·38
Pyrophosphates	$M_4P_2O_7$	2	61·92	4·76
Ditto	N″$_2$ P_2O_7	1	48·26	4·39
Borates (fused)	MBO_2	2	16·89	4·22
„ „	N″B_2O_4	1	26·5	3·79
„ „	$M_2B_4O_7$	2	49·79	3·83
„ „	N″B_4O_7	1	41·41	3·45

* N″ representing a dyad, R‴ a triad, X^{iv} a tetrad, and Y^{vi} a hexad element.

Kopp explains the difference from one another in the quotients given in the last column of the foregoing table, by the fact that the atomic heats of many of the non-metallic elements are not identical with those of the metals, and he still maintains that the molecular heat of a compound is always really the sum of the atomic heats of its constituent elements. From his own experiments he concludes that the number which represents the atomic heat of sulphur and of phosphorus is 5·4, or a little lower than the values assigned to them by Regnault, and this number, he

states, is confirmed by deducting from the experimental number obtained as the molecular heat of the sulphides and phosphides, the atomic heat of the metals which enter into their formation. By a similar process of calculation when applied to the oxides, he infers that the atomic heat of oxygen is 4, that of fluorine 5, and that of hydrogen 2·3; whilst he adopts 1·8 for that of carbon, from Regnault's experiments upon the diamond.

Amongst the most severe tests of this view are the results obtained from the atomic heats of organic compounds, some of which are given in the following table:—

Specific Heat of Organic Solids (Kopp).

Name of Substance.	Formula.	Mol. Weight.	Specific Heat.		Sp. Heat × Mol. Wt. = Mol. Heat.	
			Calculated.	Observed.	Calculated.	Observed.
Mercuric dicyanide ...	HgC_2N_2	252	0·091	0·100	22·9	25·2
Zincic potassic cyanide	$ZnK_2C_4N_4$	247·2	0·210	0·241	51·9	59·6
Potassic ferricyanide ...	$K_3FeC_6N_6$	329·3	0·227	0·233	74·8	76·7
Potassic ferrocyanide	$K_4FeC_6N_6$, 3 H_2O	422·4	0·253	0·280	106·9	118·3
Dicarbon hexachloride	C_2Cl_6	237	0·177	0·178	42·0	42·2
Cane sugar	$C_{12}H_{22}O_{11}$	342	0·340	0·301	116·3	102·9
Mannite	$C_6H_{14}O_6$	182	0·368	0·324	67·0	58·9
Succinic acid	$H_2C_4H_4O_4$	118	0·314	0·313	37·0	36·9
Tartaric acid	$H_2C_4H_4O_6$	150	0·300	0·288	45·0	43·2
Racemic acid	$H_2C_4H_4O_6$, H_2O	168	0·319	0·319	53·6	53·6
Baric formiate	Ba 2 CHO_2	227	0·135	0·143	30·6	32·5
Potassic oxalate	$K_2C_2O_4$, H_2O	184·2	0·223	0·236	41·1	43·5
Potassic trihydric dioxalate	KH_3 2 C_2O_4, 2 H_2O	254·1	0·274	0·283	69·6	71·9
Hydric potassic tartrate	$KHC_4H_4O_6$	188·1	0·261	0·257	49·1	48·3
Sodic potassic tartrate	$KNaC_4H_4O_6$, 4 H_2O	282·1	0·311	0·328	87·7	92·5
Hydric calcic malate ...	CaH_2 2 $C_4H_4O_5$, 8 H_2O	450	0·339	0·338	152·6	152·1

With the exception of the first two on the list, together with those of potassic ferrocyanide, cane sugar, and mannite, the results, calculated from the numbers assumed by Kopp as the specific heats of oxygen, hydrogen, and carbon, accord with those obtained by experiment very satisfactorily.

The specific heat of organic liquids has been studied as yet but imperfectly. It is, however, clear that the specific heat of liquids rises very rapidly with rise of temperature, and this rise stands in no simple relation to the amount of expansion which the liquid experiences. It is not therefore surprising that in the case of liquids, even when elementary, no approximation to the law of Dulong and Petit for the elements in their solid form (that the specific heat is inversely as the atomic weight) has been ascertained to exist. The specific heats of a few liquids, and

Specific Heat of Organic Liquids.

Compound.	Formula O=16.	Molecular Weight.	Sp. Heat of Equal Masses.	Mol. Heat. (Sp. heat × Mol. Weight.)
Water	H_2O	18	1·000	18·00
Wood Spirit	CH_4O	32	0·645	20·64
Alcohol	C_2H_6O	46	0·615	28·29
Amylic Alcohol ...	$C_5H_{12}O$	88	0·564	49·63
Cetylic Alcohol, Ethal	$C_{16}H_{34}O$	242	0·506	122·45
Formic Acid	CH_2O_2	46	0·536	24·66
Acetic Acid	$C_2H_4O_2$	60	0·509	30·54
Butyric Acid	$C_4H_8O_2$	88	0·503	44·26
Ether	$C_4H_{10}O$	74	0·503	37·22
Methyl Acetate ...	$C_3H_6O_2$	74	0·507	37·52
Ethyl Formiate ...	$C_3H_6O_2$	74	0·513	37·96
Ethyl Acetate... ...	$C_4H_8O_2$	88	0·496	43·65
Methyl Butyrate ...	$C_5H_{10}O_2$	102	0·487	49·67
Methyl Valerate ...	$C_6H_{12}O_2$	116	0·491	56·96
Oxalic Ether	$C_6H_{10}O_4$	146	0·457	66·72
Acetone	C_3H_6O	58	0·530	30·74
Benzol	C_6H_6	78	0·450	35·10
Oil of Mustard ...	C_4H_5NS	99	0·432	42·77
Oil of Turpentin ...	$C_{10}H_{16}$	136	0·467	63·51

their variations at different temperatures, have already been given on Regnault's authority (p. 328). In the above table, the numbers for ether, ethal, and oil of turpentin were determined by Favre and Silbermann. The remaining results are those obtained by Kopp (*Pogg. Ann.* 1848, lxxv. 98).

From these experiments, scanty and few in number though they are, it appears that the specific heat of equal masses of organic liquids decreases as the molecular weight of the substance increases; further, that when the products obtained by multiplying the specific heat into the molecular numbers are compared, this product generally increases as the molecular weight increases, and in the homologous series of the alcohols, the fatty acids, and the ethers, the increase is about 7 for each addition of CH_2 in the molecule of the compound. In the case of some metameric bodies, such as methyl acetate and ethyl formiate, the numbers for their atomic heats are alike; and ether, which has the same molecular weight as the compounds just mentioned, has the same atomic heat, though it is not metameric with them.

Latent Heat.

(174) *Disappearance of Heat during Liquefaction.*—When matter passes from the solid into the liquid state, or from the

liquid into the aëriform state, heat in large quantity disappears, and ceases for the time to affect the thermometer; hence, this modification of heat is called *latent heat.* For example, when a lump of ice at 0° C. is brought into a warm room, it gradually thaws and is converted into water; but neither the ice, nor the water in contact with it rises in temperature. So long as any portion of the ice remains unmelted, the water continues to indicate the temperature of 0°, as does also the ice. Again, a pound of water at 100° C. mixed with a pound of water at 0°, gives two pounds of water at 50°, which is the mean temperature; but a pound of ice at 0° mixed with a pound of water at 100°, gives two pounds of water, of which the temperature is only 10°·5.

In this case the water has lost 89°·5, whilst the ice has gained only 10°·5; so that 79° have disappeared, or have become latent. Hence, in order to convert a pound of ice at 0° into water at 0°, heat sufficient to raise 79 lb. of water from 0° to 1° C. is needed; that is, 79 units of heat. This heat, however, is not lost, for if the progressive cooling of water be observed in an atmosphere many degrees below the freezing-point, it will be found that the temperature of the liquid sinks regularly until it reaches 0°, when it becomes stationary, and freezing begins; the heat being supplied from that which is latent in the water. As soon as the whole has become solid, the thermometer again shows that the temperature of the mass sinks, until at length it reaches that of the surrounding air. Some idea of the quantity of heat that is required to convert ice into water, without any apparent rise in temperature, may be formed from the fact that the simple conversion of a cube of ice three feet in the side into water, also at 0°, would absorb the whole heat emitted during the combustion of a bushel of coal. (Faraday.) Pouillet has calculated that the whole of the heat of the sun's rays which fall upon the surface of the earth in the course of twelve months, would be expended in melting a layer of ice which covered the entire surface of the globe for a thickness of 101·3 feet (30·89 metres).

This large amount of heat latent in water, which is given forth as it freezes, furnishes a source of heat of the greatest value in mitigating the severity of any sudden setting in of frost, as the very act of freezing moderates the effect of the depression of temperature on surrounding objects, and renders the transition from heat to cold, and of course the converse from cold to heat, more gradual and uniform. Another very important purpose is attained by this gradual liquefaction of ice: but for this the ice that had accumulated during a long winter would at the first breeze from

the south be instantly converted into water, and sweep before it, not merely the habitations of man and their tenants, but trees, rocks, and hills. Such fearful catastrophes do now and then occur, when a volcano like Etna pours forth a stream of lava over its snow-clad sides: the flood that then ensues is even more destructive than the fiery torrent itself. The latent heat of water is greater than that of any other body, but in all cases of liquefaction there is a similar disappearance of heat; the quantity which becomes latent varying with the nature of the substance.

Person (*Ann. Chim. Phys.* 1847 [3], xxi. 295, and 1848, xxiv. 129 and 265) has determined the quantity of heat absorbed during the fusion of a considerable number of bodies, and he concludes that the latent heat of fusion is obtained by multiplying the difference between the specific heat of the substance in its liquid and its solid form by a number obtained by adding the number 160 (an experimental constant furnished by researches upon the latent heat of water) to the number of degrees Centigrade indicating the melting point of the substance in question.*

Table of Latent Heat of Liquids.

Name of Substance.	° C.	° F.	Water = 1.
Water	79·250	142 65	1·000
Sodic Nitrate	62·975	113·35	0·794
Potassic Nitrate	47·371	85·26	0·598
Zinc	28·130	50·63	0·355
Silver	21·070	37·92	0·266
Tin	14·252	25·65	0·180
Cadmium	13·580	24·44	0·171
Bismuth	12·640	22·75	0·159
Sulphur	9·368	16·86	0·118
Lead	5·369	9·66	0·068
Phosphorus	5·034	9·06	0·063
Mercury	2·840	5·11	0·036

* If l = the latent heat, d the difference of the specific heat in the liquid and in the solid state, t the melting point ° C., the latent heat may be calculated by the formula

$$(160 + t)\, d = l.$$

The results obtained with the metals do not accord with Person's theory, as the difference of their specific heats in the solid and liquid states is very trifling; but for other bodies the result calculated corresponds pretty closely with that furnished by experiment. If Person's view be correct, a consequence which he ingeniously draws from it is, that the absolute zero of temperature would fall at −160° C. (−256° F.). On the thermo-dynamical theory, the absolute zero is at −273° C. (−459°·4 F.).

The numbers in the second column of the table represent the number of degrees of temperature that an equal quantity or mass of water would be raised by the passage of each of the bodies enumerated, from the liquid to the solid state, or they may be taken as the number of pounds of water that would be raised 1° C. by the heat emitted during the congelation of one pound of each of the substances included in the table—*i.e.*, the number of units of heat: those in the third column indicate the degrees on Fahrenheit's scale to which the same weight of water would be raised by a similar experiment.

(175) *Freezing Mixtures.*—The chemist avails himself of the fact that heat disappears during liquefaction, for the purpose of procuring artificial cold: the action of freezing mixtures depends upon this principle. Many salts, while undergoing solution, produce a very considerable reduction of temperature.

For example: 100 grms. (about 4 ounces) of nitre and 100 of sal-ammoniac, each in fine powder, when mixed with 200 grms. of water, reduce the thermometer from 50° to 10° (10° to − 12° C.). Equal parts of ammonic nitrate and water reduce the temperature from 50° to 4° (10° to − 16° C.). So, likewise, equal parts of water, of powdered crystallized ammonic nitrate, and of sodic carbonate, also crystallized and in powder, effect a reduction from 50° to − 7° (10° to − 22° C.). In like manner, the solution of crystallized sodic sulphate in commercial hydrochloric acid is attended with a rapid reduction of temperature: this mixture is employed in the common refrigerators, 5 parts of the acid being poured upon 8 parts of the salt reduced to powder: the temperature may thus be reduced from 50° to 0° (10° to − 18° C.).

The most convenient mixture, however, when procurable, consists of 2 parts of pounded ice (or, better still, of fresh snow) and 1 part of common salt. A steady temperature of − 4° (− 20° C.) can by its means be maintained for many hours Again, a mixture of 3 parts of crystallized calcic chloride and 2 of snow will produce a cold sufficient to freeze mercury; if, before making the mixture, both the vessels in which the experiment is to be performed and the chloride be cooled to 32°, such a mixture will cause a thermometer when plunged into it to fall to − 50° (− 45° C.).

Even during the liquefaction of a metallic alloy by mercury, the same fact is observed; thus an alloy may be formed by melting together 207 parts of lead, 118 parts of tin, and 208 parts of bismuth; if this be granulated, by pouring it, when melted, into water, it may be dissolved in 1600 parts of mercury, and will cause a thermometer, if immersed in it, to sink from 63° to 14° (17° to − 10° C.).

It is owing to this absorption of heat during the liquefaction of solids, that not only in the melting of ice, but in the much higher temperatures required for the fusion of many of the metals, the temperature remains stationary so long as any portion of the mass remains unmelted; the excess of heat is transferred to the unmelted solid by conduction, and is rapidly absorbed by it during its liquefaction.

The following table contains the temperatures at which several substances, metallic and non-metallic, enter into fusion:—

Table of Fusing-Points.

Name of Substance.	° C.	° F.	Authority.
Mercury	−38·8	−37·9	B. Stewart
Oil of Vitriol	−35	−31	Regnault
Bromine	−7·3	18·9	"
Ice	0	32	
Phosphorus	44·2	111·5	Schrötter
Potassium	58	136·4	Regnault
Yellow Wax	61·8	143·2	Person
Sodium	97·6	207·7	Regnault
Iodine	107	224·6	Gay-Lussac
Sulphur	115	239	
Tin	232·7	451	
Bismuth	266·8	512	Person
Sodic Nitrate	310·5	591	
Lead	326·2	619	
Potassic Nitrate	339·0	642·2	
Zinc	411·7	773	
Silver	1022·8	1873	
Copper	1091·1	1996	"
Gold	1102·2	2016	Daniell
Cast Iron	1530	2786	
Wrought Iron	above 1804	above 3280	

The fusing-point of a mixture of analogous bodies is generally considerably below that of either of its separate components. Alloys, for example, often have a melting-point much below that of any of the metals which enter into their formation, as is seen in the case of fusible metal, and of the alloy of potassium and sodium, which is liquid at the ordinary temperature. It has long been practically known to the glass-maker and the metallurgist that mixtures of various silicates fuse at a temperature far below that required to melt any of them alone. A similar increase of fusibility is observed when many of the chlorides are mixed together before exposing them to heat. A mixture of equivalent quantities of sodic and potassic carbonate melts below the fusing-point of either salt separately, and is often used to effect the fusion of siliceous minerals in analysis. Schaffgotsch found that potassic acetate melts at 558° (292° C.), sodic acetate at 606° (319° C.), but a mixture of the two salts in equivalent proportions fuses at 435° (224° C.). In like manner potassic nitrate melts at 642° (339° C.), sodic nitrate at 592° (311° C.), but a mixture of the two salts in equivalent proportions liquefies

as low as 430° (221° C.), or 162° (90° C.) below the melting-point of the most fusible of the two salts.

A mixture of crystallizable fatty acids also commonly melts at a temperature below that of either when separated.

The melting-point of ice is perfectly stationary* at 0° C.; but

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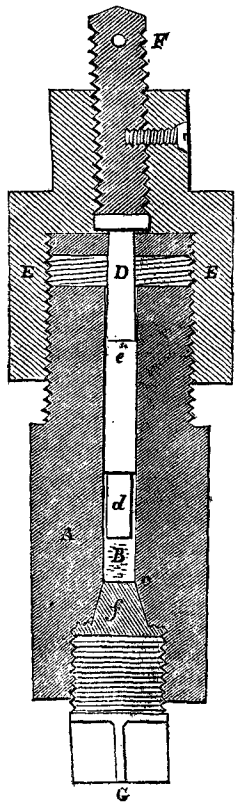
* Sir W. Thomson (*Phil. Mag.* 1850 [3], xxxvii. 123), in confirmation of the results anticipated from a mathematical investigation made by his brother, and communicated to the Royal Society of Edinburgh, January, 1849 (*Trans. Roy. Soc. Edin.* 1849, xvi. 575), found experimentally that the freezing-point of water, a liquid which *expands* at the moment of congelation, is *lowered* to a minute but measurable extent by exposing the water to pressure. Some preliminary experiments showed, that for a pressure of 8·1 atmospheres the point of congelation was lowered 0°·0588 C.: by a pressure of 16·8 atmospheres it was reduced 8°·1288: the calculated numbers being 0°·0605 and 0°·1261 respectively. At the end of the last century Dr. Hutton, in some remarks on Major Williams's experiments on the expansive force of freezing water, pointed out that preventing the expansion will prevent the freezing, and the water will remain fluid, whatever the degree of cold may be (*Trans. Roy. Soc. Edin.* 1786, ii. part 2, 27). Bunsen, on the other hand, found the melting-point of paraffin and of spermaceti to be raised by increasing the pressure. Spermaceti, for instance, under the atmospheric pressure, solidified at 117°·9 (47°·7 C.), but under a pressure of 150 atmospheres it solidified at 123°·8 (51° C.); both these bodies *contract* at the moment of solidification, and as had been anticipated by Thomson, the melting-point was *raised*. Hopkins found this to hold good for still higher pressures; his experiments comprised not only spermaceti, but also wax and stearin. The experiments of Mousson (*Ann. Chim. Phys.* 1859 [3], lvi. 252) upon this point are very remarkable. He contrived an apparatus, in which he was able to subject ice to a pressure which he estimated at 13,000 atmospheres, and by which its volume was reduced by 13 hundredths of that which it occupied at −0° C. He found that under this enormous pressure ice frozen at 0° C. remelted, and continued liquid below 0°·4 (−18° C.). This apparatus consisted of a steel bar, A, fig. 134, in the axis of which a cylindrical cavity, B, was drilled. This cavity was closed below by a conical copper plug, *f*, which was kept in its place by the screw, G. Above, the cavity was made slightly conical, and to it was fitted the copper core, *e*, upon which the steel piston, D, rested, and could be pressed down with enormous force by means of the screw, E, worked by a lever attached to the screw, F. In making the experiment, the apparatus was closed at top; it was then inverted, and a loose copper rod, *d*, was introduced, after which it was filled up to *c* with water, and subjected to a low temperature. As soon as the water was completely frozen, the plug *f* was

FIG. 134.



water which contains salts in solution has a lower point of congelation. Sea-water, for example, freezes at 27°·4 (−2°·5 C.), much of the salt separating, and purer water floating in the form of ice; whilst water which is saturated with sea-salt sinks as low as −4° (−20° C.) before freezing (71).

Rüdorff (*Pogg. Annal.* 1861, cxiv. 63) finds that in saline solutions generally, the freezing-point is below that of pure water, but the degree to which it is lowered varies with the nature of the salt employed. Almost the only salts which are well adapted to this inquiry are the chlorides and nitrates of the metals of the alkalies and alkaline earths, as few other salts possess the requisite solu-

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introduced, and the apparatus securely closed. It was then restored to its usual position, and immersed in a freezing-mixture at − 20° C. After allowing it to acquire this low temperature, the greatest degree of compression which could be applied was brought to bear upon the ice within. The ice was thus liquefied, and the copper rod, *d*, was found to *have fallen to the bottom of the water*, which immediately solidified again on relaxing the pressure. Boussingault has repeated this experiment and carried the temperature as low as − 24° without causing solidification. (*Comp. Rend.* 1871, lxxiii. 77.)

H. C. Sorby (*Proceed. Roy. Soc.* 1863, xii. 538) has made some interesting observations upon the influence of pressure upon the solubility of salts, in which he has obtained results analogous to these upon the freezing-points of liquids. He finds in cases where, as is usual, the volume of the water and of a salt after solution is less than the volume of the water and the salt separately, that the solubility is increased by pressure; but that in cases where, as when sal-ammoniac is dissolved in water, the volume of the solution is greater than that of the water and the salt taken separately, the solubility is lessened by a small but measurable amount. For sal-ammoniac this diminution for a pressure of 100 atmospheres is equal to 0·637 per cent. of the quantity of the salt in solution. Sorby calculates that the energy with which this salt tends to dissolve in a solution containing 1 per cent. less than would be dissolved without pressure is such, that any unit of salt would in dissolving give rise to a mechanical energy equal to that required to raise 171 times its own weight to the height of one metre.

On the contrary, salts which expand in crystallizing from solution must, under pressure, overcome mechanical resistance in that change, and as this resistance is opposed to the energy of crystallization, the salt is rendered more soluble. The extent of the influence of pressure, and the mechanical value of the energy of crystalline polarity, vary in different salts. For instance, a pressure of 100 atmospheres would increase the solubility of crystallized cupric sulphate as much as 3·183 per cent., whereas it would increase the solubility of sodic chloride to the extent of only 0·419 per cent. The energy with which this latter salt tends to crystallize from a solution containing 1 per cent. more than would be dissolved without pressure is such, that any unit of salt in dissolving would give rise to a mechanical energy sufficient to raise 157 times its own weight to the height of one metre; whereas, in the case of cupric sulphate, this energy is only sufficient to raise 7 times its own weight to the same height. Of course, if the solution were still more supersaturated, the energy of crystallization would be greater, and *vice versâ*.

bility at low temperatures. In the case of salts which furnish anhydrous crystals, so far as can be judged from the limited number of salts submitted to experiment, the depression of temperature is directly proportional to the quantity of salt present in the liquid. For example, successive additions of 1 per cent. of each of the following salts produce a successive reduction of the freezing-point to the following extent:—

Name of Salt.	° F.	° C.
Sal-ammoniac	1·175	0·653
Sodic chloride	1·080	0·600
Potassic chloride... ...	0·797	0·443
Ammonic nitrate... ...	0·691	0·384
Sodic nitrate	0·666	0·370
Potassic carbonate ...	0·570	0·317
Calcic nitrate	0·498	0·277
Potassic nitrate	0·480	0·267

It would appear that salts which crystallize with water cause a depression in proportion to the amount of hydrated salt dissolved. Calcic chloride occasions a depression of the freezing-point of 0°·408 (0°·227 C.) for each addition of 1 per cent. of the salt $CaCl_2$, 6 H_2O; baric chloride a depression of 0°·345 (0°·192 C.) for each addition of 1 per cent. of the compound $BaCl_2$, 2 H_2O. Sodic chloride crystallizes below 14° F. (−10° C.) with 2 H_2O; but these crystals are rapidly dehydrated as soon as the temperature rises above that point: it is remarkable that, for all temperatures above −10° C., the depression of the freezing-point is proportional to the quantity of *anhydrous* salt in the solution, but below −10° it is proportionate to the addition of the *hydrated* salt NaCl, 2 H_2O, the depression being equal to 0°·615 F. (0°·342 C.) for every addition of 1 per cent. of this hydrate to the solution.

In the process of freezing as it usually occurs in nature, the act of solidification goes on, not continuously, but in successive layers, and in the intervals between these layers is a stratum of ice slightly more fusible than the mass either above or below. This is beautifully seen by placing a block of homogeneous transparent ice, such as that from the Wenham Lake, in the sun's rays after concentrating them by a large convex lens. Immediately that this is done, the interior of the mass becomes filled with little flower-shaped figures, each flower having six petals, evidently composed of water, while in the centre is a spot which shines with metallic brilliancy, and which looks like an air-bubble, but is

really a space filled only with aqueous vapour, and produced in consequence of the circumstance that water occupies a smaller volume than the ice which furnished it. These little flowers occur in horizontal planes parallel to the surface of congelation.* —(Tyndall, *Phil. Trans.* 1858, 211.) Faraday has suggested what seems to be a very probable explanation of these successive planes of freezing—viz., the separation of saline particles from each layer of water as it is frozen (71), so that the salts accumulate below the stratum first frozen, and form a very dilute saline solution, the freezing-point of which is a fraction of a degree below that of pure water; this thin stratum when frozen furnishes a layer of ice more fusible than the rest; a fresh layer freezes beneath, gradually excluding its saline particles, which again accumulate below, forming a fresh more fusible layer, and so on successively.

(176) *Regelation of Ice.*—It was remarked some years ago by Faraday, that when two pieces of ice at 0° C., with moistened surfaces, are placed in contact, they freeze together, and manifest the phenomenon thence designated as the *regelation* of ice; whereas, if the surfaces be dry, they do not cohere. It is owing to this circumstance that during a thaw the particles of snow cohere firmly into a solid lump, whilst during a frost there is difficulty in forming the dry particles into a compact mass. This regelation of ice will occur when the surfaces of the blocks are in contact, even though the external air may be at a temperature of 25° or 30° C., or even when the ice is immersed in water at this temperature. Certain solids, as flannel, hair, or cotton, will freeze to ice even in a warm atmosphere, though others, such as saline substances, gold leaf, and the metals, will not thus freeze to it. Tyndall has followed up these observations, and made some interesting experiments and deductions from them. He took a sphere of transparent ice, and placed it in a warm room under a small hydraulic press between two pieces of boxwood hollowed out so as to form a flattened lenticular cavity. The ice broke, but, on continuing the pressure, it froze again, and in less than a minute was converted into a flattened, *transparent,* lenticular mass. This mass was in turn placed in a shallow cylindrical cavity of boxwood and again submitted to pressure; again it was crushed and became reduced to the form of a flat transparent cake; and this again was placed in a hemi-

* In certain exceptional cases this parallelism is disturbed. Probably this is due to the breaking-up of the original floe, and consolidation of its fragments irregularly, by subsequent regelation.

spherical cavity in the wood and subjected to the pressure of a hemispherical plug which fitted the cavity; a third time it was crushed, and after a few seconds it froze again into a transparent cup of ice.* Tyndall considers that upon the theory that heat is the result of vibratory motion, the liquefaction of ice, when perfectly homogeneous, must necessarily take place more easily upon the surface than within the mass; and conversely, the freezing of a thin layer of water between two masses of ice should occur more readily than upon the surface of a single mass, and hence he attempts to account for regelation. The explanation appears, however, to be insufficient; since, if true for ice, it should hold good for all substances solidifying after fusion, when two portions of the solid are brought into contact beneath the still liquid mass; and it offers no explanation of the freezing of ice to flannel, which apparently is due to the same cause as the freezing of ice to ice. It has been supposed that the masses of ice are colder within than at the surface, and hence that regelation is the result of the absorption of heat by the internal portions. Tyndall has, however, proved conclusively that this hypothesis is at variance with facts, and is indeed impossible from the conducting nature of ice itself. The ingenious theory of James Thomson, that regelation is due to the lowering of the freezing-point by the mutual pressure of two masses of ice, and that the absorption of heat due to this liquefaction freezes the contiguous layer of water, is also quite inadequate

* These observations have been ingeniously applied by Tyndall to account for the motion of glaciers. These frozen rivers of ice, in descending from the mountain sides, constantly have to force their way through contracted gorges in the rock, and gradually flow onwards, melting away at their base, whilst fresh portions of ice are forced downwards from the upper regions of the mountain by the weight of the superincumbent ice. It was ascertained by Prof. J. D. Forbes, in a series of beautiful observations, that during the descent of the glacier through its channel, the central portions of the mass move more quickly than the portions on its sides: and he likened the flow to the descent of a viscous liquid, and propounded what has been known as the viscous theory of glacier motion. Viscosity, however, is not a property which is exhibited by ice; and Tyndall has shown that all the phenomena of glacier motion are accurately accounted for by this process of crushing, and subsequent regelation into solid transparent ice. Graham has since suggested that ice may exist in two conditions—the crystalline, which is brittle, and the vitreous or colloid, in which it possesses a certain viscosity. (*Phil. Trans.* 1861, 222.) This view, however, as yet remains unsupported by direct experiments. Ice just at the freezing-point is, however, less hard than when it is reduced to a lower temperature; and the experiments of Person (*Ann. Chim. Phys.* 1850 [3], xxx. 73) show a continued evolution of latent heat by ice as it is cooled a few degrees below 0° C., which is probably connected with a molecular change subsequent to the first freezing.

to account for the effect, even if pressure were a necessary element in effecting regelation, which Faraday and others have shown it is not. At present therefore the phenomenon needs further elucidation.

(177) *Evolution of Heat during Solidification.*—When liquids return to the solid form, their latent heat is again given out. Water, if undisturbed, may be cooled down in a narrow tube even 10° C. below the freezing-point without congealing; but the least agitation causes a portion to solidify suddenly, and the latent heat emitted at the moment by the portion which freezes raises the temperature of the whole mass to 0° C. According to Dufour, this cooling of water below its freezing-point is easily effected by suspending the water in the midst of a liquid of the same density as itself, such as a mixture of chloroform and oil of almonds in suitable proportions, and exposing them to the cold of a freezing-mixture: contact with a fragment of ice causes the instant solidification of the water, though agitation, or stirring with a metallic rod, does not always do so. In like manner, sulphur, or phosphorus, if suspended in solution of zincic chloride, remains liquid many degrees below its point of solidification until touched with a fragment of its own substance. Acetic or sulphuric acid, as well as many other substances, admits, like water, of being cooled down several degrees below its point of solidification; but if agitated, or if touched with a portion of its own substance in the solid form, it immediately solidifies with evolution of heat. When sulphur vapour is condensed on glass, small drops are formed which often remain liquid for days.

A similar evolution of heat occurs when a supersaturated solution of sodic sulphate (73) is made to crystallize suddenly by agitation, the mass becoming sensibly warm to the hand. The solidification of metallic bodies is attended with a like evolution of heat.

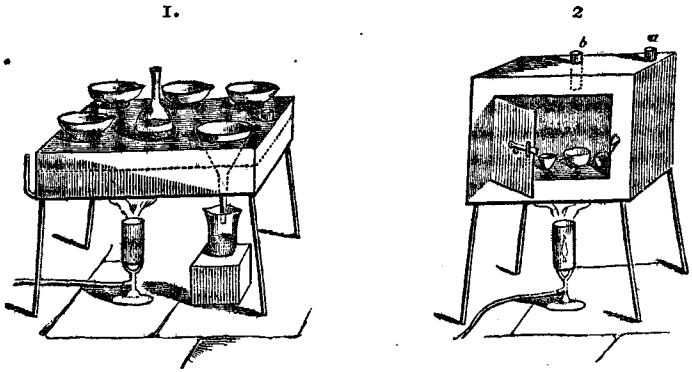
(178) *Disappearance of Heat during the Formation of Vapour.*—In the change from the liquid to the gaseous state, the disappearance of heat is found to occur to an extent still greater than in the liquefaction of a solid. A vessel containing water, such as the boiler of a common still, if placed over a source of heat which is tolerably uniform in temperature, receives in equal times nearly equal accessions of heat; the water at first rises steadily in temperature, but at length it boils, and the thermometer becomes stationary: no matter how much the heat be urged, provided that the steam be allowed to escape freely, the temperature of the boiling liquid cannot be raised beyond a

certain point. If the vapour be made to pass through the worm of the still, which is cooled by immersion in water, the steam will transfer part of its heat to the water in the condenser, which rises rapidly in temperature, whilst the vapour returns to the liquid form; but the quantity of water that is raised in the worm-tub to nearly 100° C. is very much greater than the quantity that is condensed into the form of liquid in the receiver of the still.

The large amount of latent heat contained in steam, renders it possible to use steam as a convenient and economical mode of warming buildings and apparatus which do not require to be raised to a temperature beyond that of boiling water. In practice it is found convenient, in warming a building which is used for domestic purposes, to allow one square foot of radiating surface in the steam-pipe for every 200 cubic feet of space to be heated. This estimate, however, is liable to modification, because the greater the extent of radiating and conducting surface exposed by the windows in proportion to the cubic contents of the apartment may be, the more rapid is the loss of heat.

The maintenance of a steady temperature which cannot rise above 100° C., is often required in the laboratory in the prosecution of various inquiries, especially in such as relate to organic chemistry, and for this purpose a small steam-bath, such as is represented at 1, fig. 135, is extremely useful; it may also be

FIG. 135.



employed to assist in effecting the filtration of hot liquids, where it is important to maintain their high temperature. In drying organic substances, a kind of double oven, or hot closet, made of copper, as exhibited at 2, is a convenient mode of applying heat; the interval between the internal and external plates of copper is filled with water which is heated by the gas flame below; if a higher temperature than this be required, the interval may be filled with oil; the temperature in the latter case may be regulated by a thermometer, introduced at *a*; at *b* is a tube for the escape of vapour; this tube communicates with the drying chamber.

(179) *Ebullition.*—The gradual absorption of heat in the passage from the liquid to the gaseous state is not less essential to the comfort, and even to the existence of man, than the corresponding absorption in the passage from the solid to the liquid

Table of Boiling-Points and Densities of Liquids.

Substances used.	Boiling Pt. ° C.	Boiling Pt. ° F.	Density at 0° C.	Authority.
Sulphurous Anhydride	−8·0*	17·6	1·4911†	Pierre
Ethyl Chloride	11·0	51·8	0·9214	„
Methyl Bromide	13·0	55·4	1·6644	„
Aldehyd	20·8	69·4	0·8009	Kopp
Methyl Formiate	33·4	92·1	0·9984	„
Ether	34·9	94·8	0·7365	„
Ethyl Bromide	41·0	105·8	1·4733	Pierre
Methyl Iodide...	44·1	111·4	2·1992	„
Carbonic Disulphide	48·0	118·4	1·2931	„
Formic Ether	53·1	127·6	0·9357	„
Acetone	56·3	133·3	0·8144	Kopp
Methyl Acetate	56·3	133·3	0·9562	„
Silicic Chloride	59·0	138·2	1·5237	Pierre
Bromine	63·0	145·4	3·1872	„
Wood Spirit	65·5	149·9	0·8179	Kopp
Ethyl Iodide	70·2	158·5	1·9755	Pierre
Acetic Ether	73·8	164·9	0·9069	„
Alcohol	78·4	173·1	0·8151	„
Trichloride of Phosphorus ...	78·5	173·4	1·6162	„
Benzol	80·4	176·8	0·8991	Kopp
Dutch Liquid	84·8	184·7	1·2803	Pierre
Methyl Butyrate	95·9	204·6	0·9209	Kopp
Water	100·0	212·0	1·0000	„
Formic Acid	105·3	221·5	1·2227‡	„
Butyric Ether...	114·8	238·7	0·9041	„
Stannic Chloride	115·6	240·0	2·2671	Pierre
Methyl Valerate	116·2	241·2	0·9015	Kopp
Acetic Acid	117·3	243·1	1·0800§	„
Fusel Oil...	132·1	269·8	0·8271	Pierre
Ethylene Dibromide	132·7	270·9	2·1629‖	„
Arsenious Chloride...	133·9	273·0	2·2050	„
Titanic Chloride	135·9	276·6	1·7609	„
Silicic Bromide	153·3	308·0	2·8128	„
Butyric Acid	157·0	314·6	0·9886	Kopp
Sulphurous Ether	160·3	320·4	1·1063	Pierre
Phosphorous Bromide	175·3	347·5	2·9249	„
Sulphuric Acid	337·8	640·0	1·8540	Marignac
Mercury	350 0	662·0	13·5960	Regnault

condition. Were it otherwise, every attempt to boil a saucepan or a flask of water or other liquid would be attended with explosion, from the sudden formation of vapour, the moment that the boiling-point was attained.

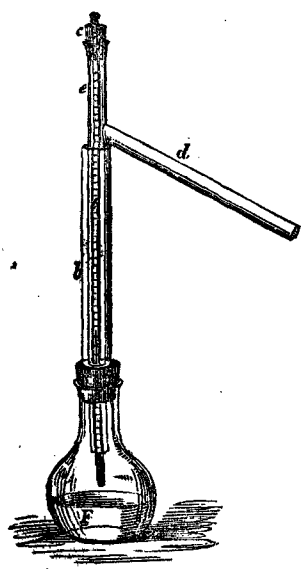
* 10°·5 C. Bunsen. † At −20°·5. ‡ 1°·2067 at 13°·5.
§ 1°·0619 at 17°. ‖ At 20°·7.

By the term *ebullition*, or boiling, is meant the formation, in any liquid, of bubbles of vapour of a pressure equal to that of the superincumbent atmosphere at the time.

Although the boiling-point of each liquid, *cæteris paribus*, is always fixed, yet different liquids vary quite as much in the temperature at which this change occurs, as solids do in their points of liquefaction. This is shown by a glance at the preceding table, which contains the boiling-points of a number of liquids, recently determined with very great care, reduced to the atmospheric pressure of $760^{mm.}$ of mercury: the densities of the liquids at 0° C. are also given.

The process of ebullition may be beautifully shown in a common glass flask, heated from below. At first, bubbles of vapour are formed at the bottom of the vessel; these bubbles are condensed and disappear with a peculiar vibratory sound before they reach the surface; at length the temperature of the whole mass of liquid becomes nearly uniform, and the bubbles of steam as they are formed rise to the surface and break, emitting a perfectly transparent, invisible vapour, which does not become condensed into the cloudy form commonly but erroneously designated as steam, until its temperature has been sufficiently reduced by the external air to bring it back to the liquid form in exceedingly minute globules.

FIG. 136.



The temperature at which any given liquid boils, although perfectly fixed under certain conditions, is nevertheless influenced by several circumstances, such as—1, the nature of the vessel in which it is boiled; 2, the presence of matters in solution in the liquid; and 3, and most important of all, the variation of the pressure of the atmosphere upon its surface.

The boiling-point of a liquid constitutes one of its most important physical characters, and is often the surest guarantee of its freedom from admixture with other bodies. The use of a simple expedient enables the boiling-point of a valuable liquid to be determined without loss, upon small quantities of the substance under trial.

In fig. 136, F is a small flask which contains the liquid, *t* the thermometer passing through the cork *c*, and enclosed in a long tube *e*, which fits into a cork adjusted to the neck of the flask F: *b* is an outer tube to prevent the premature condensation of the vapour, *d* a lateral tube for carrying off any part of the liquid which may distil over; by this arrangement the bulb and the whole stem of the thermometer is immersed in the vapour of the boiling liquid, and an accurate observation may be made with little difficulty, due attention being paid in all cases to the barometric pressure at the time.

(180) 1. *Influence of Adhesion on the Boiling-Point.*—Adhesion of the liquid to the surface of the vessel which contains it has a marked effect in raising the boiling-point. In consequence of this action, water sometimes boils at 101° C. in a glass vessel, but the temperature falls to 100°, and continues to boil steadily at this point, if a pinch of metallic filings be dropped in. If the interior of the vessel be varnished with shell-lac, the boiling will often not occur till a temperature of 105° C. is reached, and then will take place in bursts, the temperature falling to 100° at each gust of vapour. So again the presence of a little oil elevates the boiling-point of water 2° or 3° C. The experiments of Donny have thrown light upon some of the causes by which ebullition is facilitated. He has found that the presence of air in solution singularly assists the evolution of vapour. From the increased pressure which the dissolved air acquires by the addition of heat, minute bubbles are thrown off in the interior of the liquid, especially where it is in contact with a rough surface; and into these bubbles the steam dilates and rises. By long boiling of the water, the air becomes nearly all expelled; in such a case the temperature has been observed to rise even as high as 360° (182° C.) in an open glass vessel, which was then shattered with a loud report, by a sudden explosive burst of vapour. In such circumstances the cohesion retains the particles of the liquid throughout the mass in contact with each other, in a species of unstable equilibrium; and when this equilibrium is overturned at any one point the repulsion of the excess of heat stored up in the mass suddenly exerts itself, and the result is an explosion with the instantaneous dispersion of the liquid. The difficulty of expelling air completely, even from a small quantity of water, can be adequately conceived by those only who have attempted it; ebullition *in vacuo* for a very considerable period is not sufficient to effect it. In the slow freezing of water the air previously held in solution is perfectly expelled. In consequence of this absence

of air, if a lump of ice free from air-bubbles be immersed in heated oil, so as to melt it without allowing it to come into contact with air, the temperature of the water may be raised many degrees above its boiling-point, and it will then be suddenly converted into steam with an explosion. Dufour finds that many liquids may be heated far beyond their normal boiling-point by suspending them in the midst of a liquid of equal density, but which can be heated sufficiently without itself beginning to boil. If the globule of suspended and superheated liquid be touched with any solid body, it bursts into vapour with an explosion.

Where the latent heat of the vapour is low, and the liquid has comparatively little adhesion to air, as is the case with alcohol, or ether, or sulphuric acid, frequent bumping or irregular boiling occurs, endangering the vessel and its contents.

(181) 2. *Influence of the Solution of Solids in a Liquid, on its Boiling-Point.*—Any cause that acts in opposition to the repulsion of heat produces a corresponding rise in the boiling-point; so that the solution of a salt in water, by the influence of adhesion, always elevates the point of ebullition, and the more so the larger the quantity of salt added. Indeed, it has been supposed that the quantity of salt required to produce a certain rise of temperature might be employed as a measure of the amount of adhesion between the liquid and the salt in solution. Legrand (*Ann. Chim. Phys.* 1835 [2], lix. 423) has published a series of careful experiments upon seventeen different salts, and the results which he has obtained possess considerable interest.

It might be supposed, since the pressure of vapour increases with the temperature, that the addition of a larger quantity of salt would be required to raise the boiling-point from 101° to 102° than from 100° to 101° C. In only three cases, however, was this effect produced; these three salts stand first in the following table. In six instances the effect produced was exactly the reverse: whilst in the seven instances which stand lowest in the table, the successive quantities of salt which it was requisite to add in order to produce a successive rise in the boiling-point of 1° decreased up to a certain point, and beyond this steadily increased. The salts employed were all used in the anhydrous state—that is to say, they were dried so as to be entirely deprived of their water of crystallization before being dissolved.

Notwithstanding their high boiling-point, the vapour which rises from such solutions adjusts itself almost immediately to the

atmospheric pressure, and is not permanently hotter than the steam of boiling water, as Faraday and Magnus have shown.

In separating bodies by fractional distillation it is therefore necessary to maintain the bulb of the thermometer in the vapour, and not in the boiling liquid, since in the latter case the temperature indicated would give no information of the boiling-point of the liquid distilling.

Influence of Salts in Solution on the Boiling-Point of Water.

Name of the Salt.	Quantity of salt required to raise the boiling-point of 100 parts of liquid		Boiling-point of a saturated solution.		Quantity of salt in 100 parts of water in saturated solution.
	From 212° to 213°·8 F. (100° to 101° C.)	From 213°·8 to 215°·6 F. (101° to 102° C.)	° C.	° F.	
Sodic Nitrate	9·3	9·4	121	249·8	224·8
Ammonic Nitrate ...	10·0	10·5			unlimited
Potassic Nitrate ...	12·2	14·2	115·9	240·6	335·1
Potassic Chlorate ...	14·6	14·6	104·2	219·6	61·5
Sodic Chloride... ...	7·7	5·7	108·4	227·1	41·2
Potassic Chloride ...	9·0	8·1	108·3	226·9	59·4
Sodic Carbonate ...	14·4	12·3	104·6	220·3	48·5
Sodic Acetate	9·9	7·7	124·4	255·9	209·0
Baric Chloride	19·6	12·9	104·4	219·9	60·1
Hydric disodic Phosphate	21·0	19·8	106·6	223·9	112·6
Sal-Ammoniac	7·8	6·1	114·2	237·6	88·9
Calcic Chloride... ...	10·0	6·5	179·4	355	325·0
Potassic Acetate ...	10·5	9·5	169·0	336·2	798·2
Potassic Carbonate ...	13·0	9·5	135·0	275	205·0
Calcic Nitrate	15·0	10·3	151·0	303·8	362·2
Strontic Chloride ...	16·7	8·5	117·8	244	117·5
Potassic Nitrate ...	26·9	20·3	114·4	238	296·2

On comparing together solutions which contain equal quantities of different salts, it will be found that the most soluble salts are by no means uniformly those which produce the greatest elevation of the boiling-point. A solution containing 40 per cent. of common salt (very nearly saturated) boils at 226°·4 (108° C.); whilst in the case of nitre (a far more soluble salt) a solution of the same strength boils at 219°·2 (104° C.).

(182) 3. *Influence of Pressure on the Boiling-Point.*—Since ebullition consists essentially in the rapid formation of vapour of a pressure equal to that of the atmosphere which is exerting its pressure on the surface of the liquid, any diminution of that pressure should be attended with a corresponding depression of the boiling-point; and it is a fact that water which has long ceased to boil under the usual atmospheric pressure, may be at

once made to enter into ebullition by placing it under the receiver of the air-pump, and exhausting the air; by this means water may be made to boil at a temperature of 70° (21° C.). Indeed liquids in general boil *in vacuo* at from 60° to 140° (33° to 77° C.) below their ordinary point of ebullition when under a barometric pressure of 760^{mm}.

This result may be shown by boiling some water in a Florence flask, and corking up the flask whilst the steam is escaping rapidly. Upon pouring cold water over the upper part of the flask the steam is condensed, its pressure is removed, and the water begins to boil briskly; but in this case the bubbles nearly all rise from the surface, not from the bottom of the liquid. A simple proof that steam from boiling water possesses an elasticity equal to that of the atmosphere is obtained by repeating the last experiment with a tin canister instead of a globular flask. On corking up the canister and pouring cold water over it, the steam within is suddenly condensed, a vacuum is produced, and the canister is crushed in by the pressure of the external air.

The reduction of temperature at which boiling takes place is advantageously applied in the preparation of vegetable extracts the medicinal properties of which would be impaired by the ordinary temperature of 100° C., and by exposure to the air. The apparatus consists of a still and a receiver, which are connected by an air-tight joint, and are filled with steam to expel atmospheric air, and then hermetically sealed; on cooling the receiver, rapid evaporation and ebullition take place at a temperature much lower than that of the usual boiling-point of the liquid. A modification of this process is used in the manufacture of sugar, both in the concentration of the cane-juice and in the subsequent evaporation of the syrup.

(183) *Measurement of Heights by the Boiling-Point.*—As might be expected in consequence of the diminution of atmospheric pressure, it is found that on ascending from the earth's surface the temperature at which water boils becomes gradually lower. In descending a mine the effect is reversed, and the boiling-point becomes proportionately elevated. De Saussure observed that on the summit of Mont Blanc, which is 15,650 feet (nearly three miles) above the sea-level, water boils at 185°·7 (85°·4 C.); and Wisse determined the boiling-point upon Mount Pichincha, at an altitude of 15,668 feet (4775·6 metres), to be 185°·29 (85°·16 C.) whilst the barometer stood at $437^{mm}·6$. The observation of the point at which water boils at any particular elevation furnishes an easy means of determining its altitude above the sea-level; a difference of about 327 metres in elevation produces a variation of 1° C., or 596 feet of ascent produces a variation of 1° F. in the boiling-point of water.

The following table shows the temperature at which water boils at the corresponding heights of the barometric column, calculated by Regnault, and confirmed by direct observation:—

*Boiling-Points of Water at different Pressures.**

Boiling Pt. ° F.	Barometer. Inches.	Boiling Pt. ° F.	Barometer. Inches.	Boiling Pt. ° F.	Barometer. Inches.
184	16·676	195	21·124	206	26·529
185	17·047	196	21·576	207	27·068
186	17·421	197	22·030	208	27·614
187	17·803	198	22·498	209	28·183
188	18·196	199	22·965	210	28·744
189	18·593	200	23·454	211	29·331
190	18·992	201	23·937	212	29·922
191	19·407	202	24·441	213	30·516
192	19·822	203	25·014	214	31·120
193	20·254	204	25·468	215	31·730
194	20·687	205	25·992	216	32·350

Boiling Pt. ° C.	Barometer. Millimetres.	Boiling Pt. ° C.	Barometer. Millimetres.	Boiling Pt. ° C.	Barometer. Millimetres.
85	433·04	90·5	535·53	96	657·54
85·5	441·62	91	545·78	96·5	669·69
86	450·34	91·5	556·19	97	682·03
86·5	459·21	92	566·76	97·5	694·56
87	468·22	92·5	577·50	98	707·26
87·5	477·38	93	588·41	98·5	720·15
88	486·69	93·5	599·49	99	733·21
88·5	496·15	94	610·74	99·5	746·50
89	505·76	94·5	622·17	100	760·00
89·5	515·53	95	633·78	100·5	773·71
90	525·45	95·5	645·57	101·0	787·63

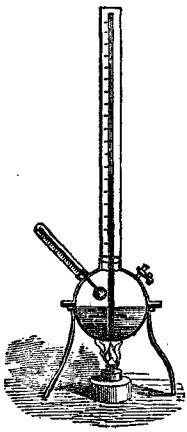
The necessity of attending to the height of the barometer at the time of making a careful observation upon the boiling-point of any liquid will now be obvious. It has been ascertained that at pressures near $760^{mm.}$ of mercury a variation in the height of the barometric column of about $2{\cdot}7^{mm.}$ makes a difference of $0^{\circ}{\cdot}1$ C., or that of one-tenth of an inch in the barometric column makes a difference of more than a sixth of a degree F. in the boiling-point; so that within the range of the barometer in this climate the boiling-point of water may vary nearly 3° C., or 5° F.

(184) *High-Pressure Steam.*—As a reduction of the pressure lowers the boiling-point, so an augmentation of the pressure raises it. To demonstrate this fact an apparatus has been contrived, consisting of a small iron boiler (fig. 137), furnished with three apertures in the lid, through one of which a thermometer

* For an extended table of this kind, vide Regnault, *Ann. Chim. Phys.* 1845 [3], xiv. 206; or Dixon *On Heat*, p. 269.

stem is passed air-tight; through the second, a long glass tube open at both ends is inserted; the lower extremity of this tube plunges below the surface of mercury placed in the boiler, above which a quantity of water is introduced; the third aperture must be furnished with a stop-cock. It will be found, on applying heat, that so long as free communication with the atmosphere is permitted through the open stop-cock, the temperature of ebullition will remain steadily at 100° C.; but by closing the cock, the steam may be confined, and as fresh portions of steam continue to rise from the water, the pressure on the surface increases, as is shown by the rise of the mercury in the open tube; the boiling-point also becomes higher; until when the mercury stands at $760^{mm.}$, or 30 inches, and the pressure on the surface is equal to that of an additional atmosphere, the thermometer marks a temperature of 120°·8 C. By continuing the heat without allowing the steam to escape, the boiling point rises still higher and the pressure of the steam increases with increasing rapidity as the temperature rises, as is shown by the following table, founded on the experiments of Regnault:—

FIG. 137.



Temperature of Steam at High Pressures.

Pressure in atmospheres of 30 inch mercury.	Temp.		Rise in temp. ° F. for each additional atmosphere.	Pressure in atmospheres of 30 inch mercury.	Temp.		Rise in temp. ° F. for each additional atmosphere.
	° C.	° F.			° C.	° F.	
1	100	212·0	°	11	184·6	364·3	°
			37·5				6·8
2	120·8	249·5	23·8	12	188·4	371·1	6·7
3	134·1	273·3	17·9	13	192·1	377·8	6·2
4	144	291·2	14·8	14	195·6	384·0	6·0
5	152·2	306·0	12·2	15	198·9	390 0	5·4
6	159	318·2	11·3	16	201·9	395·4	5·4
7	165·3	329·5	9·9	17	204·9	400·8	5·1
8	170·8	339·4	9·0	18	207·7	405·9	4·8
9	175·8	348·4	8·1	19	210·4	410·7	4·7
10	180·3	356·5	7·8	20	213	415·4	

These results differ but little from those obtained under the direction of Dulong and Arago, by a commission appointed for the purpose many years ago by the French Government. They found the temperature of steam of 20 atmospheres to be 417°·4 (214°·2 C.), and calculated that if the pressure rose to 50 atmospheres the temperature would amount to 510°·4 (265°·8 C.).

It will be observed that the increase of pressure, for equal increments of temperature, is more rapid at high than at low temperatures, and this circumstance (in addition to the greater simplicity of construction of the machinery in high-pressure engines) is one of the principal reasons for the increased economy of power obtained in employing high-pressure steam as a motive power, when compared with that furnished by the use of low-pressure engines. But it is only when in contact with a body of water from which fresh steam is constantly rising, that the pressure augments in this manner, and thus is sufficient to rend asunder the strongest boilers. If dry steam alone be heated, it follows the law which regulates the expansion and pressure of gaseous bodies in general (134, 197).

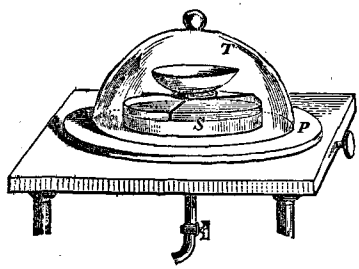
High-pressure steam whilst confined is always of the temperature of the water from which it is produced; it is, therefore, often used in the arts to supply a steady temperature above that of 100° C. It is found that the solvent powers of water are much increased by the elevation of temperature caused by preventing the free escape of the steam. Papin's digester is an apparatus designed to effect this object; it is simply a strong iron vessel, furnished with a safety-valve for regulating the pressure at which the steam is allowed to blow off. The water may thus be kept steadily at any required temperature above 100° as long as is requisite. The gelatin of bones may by this means be easily extracted from the earthy matter, although the bones may be boiled for hours in water at 100° C. without undergoing any such change.

(185) *Production of Cold by Vaporization.*—In all cases, whether volatilization occur above the usual boiling-point or below it, heat is absorbed in large quantity. If a few drops of ether be allowed to fall on the hand, the liquid disappears rapidly in vapour, and produces the sensation of cold. Indeed, the boiling of one liquid may be attended with the freezing of another which is brought into its vicinity. Place, for example, a drop or two of water between two watch-glasses, pour a little ether into the upper glass, and, having introduced them into the receiver of the air-pump, exhaust the air; the ether will speedily boil, and the water between the two glasses will be frozen, by the rapid abstraction of heat which it has experienced during the conversion of the ether into vapour.* Water, as Leslie has shown, may even be

* Mr. Harrison has contrived an ingenious freezing-apparatus upon this principle: one form of the instrument is figured in the *Pharmaceutical Journal*

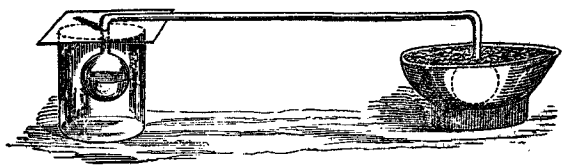
frozen by the rapid absorption of heat occasioned by its own evaporation. This experiment may be performed by supporting a watch-glass (T, fig. 138) containing water, over a dish of oil of vitriol, S, under the receiver of the air-pump, P. A piece of cork hollowed at its upper surface, and charred by being placed in a flame, furnishes a good support for the water in consequence of its being a bad conductor of heat. On exhausting the air, the water evaporates quickly, the vapour being removed with great avidity by the oil of vitriol as fast as it is formed; and in two or three minutes the water which remains in the watch-glass becomes converted into ice.

FIG. 138.



Water is also frozen by its own evaporation in the *Cryophorus*, which derives its name from κρύος, frost, φορὸς, bearing, in allusion to its mode of action;

FIG. 139.



condensation of the vapour being effected by the application of a freezing-mixture, at a distance from the evaporating surface. The apparatus consists of a long

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(1857, xvi. 477). About ten gallons of ether are placed in a small metallic multitubular boiler, which is immersed in a strong solution of salt and water, contained in a wooden trough cased in a non-conducting material. The boiler is connected with an exhausting pump, by working which the ether is caused to evaporate rapidly, and the temperature of the boiler is proportionably reduced, at the expense of that of the salt water around it. This salt water is made to flow off gradually, through a channel containing a series of metallic vessels, each capable of containing 14 or 15 lb (5 or 6 kilogr.) of the water to be frozen. The salt water, which is reduced at first to a temperature of about $-4°.5$, is returned again by a small pump when its temperature has risen to about $-2°$ C.: and it is again made to flow around the boiler in which the ether is evaporating, so that a perpetual circulation of cold salt water is maintained: the ether, the volatilization of which has caused the reduction of temperature, is condensed in a worm by means of a current of cold water, and is returned, with scarcely any loss to the boiler. Mr James Young found in working the apparatus on a large scale that, for every ton of coal consumed in working the pumps, 1 ton of ice was produced, though this probably is not by any means the maximum quantity of ice which the apparatus could produce by suitable

glass tube bent twice at right angles, and terminating in a bulb at each extremity; as shown in fig. 139. In making the instrument, one of these bulbs is partially filled with water, which is then made to boil briskly; the steam thus generated expels the atmospheric air through a capillary opening left in the other bulb, and when the instrument is thus freed from air, and filled only with water and vapour of water, the aperture is sealed. To make use of it, the water is all collected into one bulb, and the empty bulb is plunged into a freezing-mixture; the aqueous vapour which this bulb contains is thereby condensed, and evaporation occurs rapidly from the surface of the liquid in the other bulb; its sensible heat is thus diminished, and the water in a few minutes begins to freeze. The bulb containing the water should be protected from currents of air by enclosing it in a glass, as shown in the figure.

(186) *Measurement of the Latent Heat of Vapours.*—Equal masses of different liquids require very different quantities of heat to convert them into vapour. The quantity of heat which is thus rendered latent may be determined by distilling over a given mass of the liquid, and condensing it in a large volume of water, the temperature of which is noticed before and after the experiment. Suppose the latent heat of steam to be 536° C.; a litre of water converted into steam would on recondensation raise the

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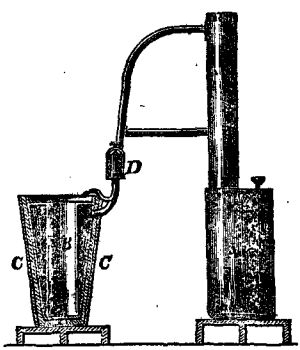
improvements in the mounting. A simpler form of apparatus, in which the evaporation of ammonia is made use of for the production of a low temperature, was exhibited in London at the International Exhibition of 1862 by MM. Carré and Co.

Fig. 140 represents the apparatus: A is a strong boiler of wrought iron, filled for three quarters of its capacity with a concentrated solution of ammonia; B, a wrought iron annular condenser, shown in section, connected with the boiler by pipes specially arranged with a view to prevent the liquid from boiling over into the receiver. In order to use the instrument, the boiler is laid upon its side, with the condenser upwards, for about ten minutes, so as to allow all the liquid to drain back into the boiler, the expulsion of the liquid being facilitated by heating the condenser with a lamp. The boiler is then heated very gradually by means of a stove or large gas-burner, and the condenser plunged into a vessel of cold water, through which a stream of cold water is kept running. A little water is placed in the cup, D, in the bottom of which is a screw-cock communicating with the interior. Distillation is next proceeded with, until the temperature of the boiler has risen to about 270° (132° C.), when the ammonia will have been in a great measure expelled from the liquid, and condensed in the receiver under the pressure of its own particles. The boiler is then withdrawn from the fire, the water in the cavity, B, is allowed completely to drain away, a cork is put into the hole at the bottom of the space, B, and a little alcohol is poured into the cavity, after which the vessel containing the water to be frozen is introduced. The boiler is plunged into a vessel of cold water, and kept cool by a rapid current of cold

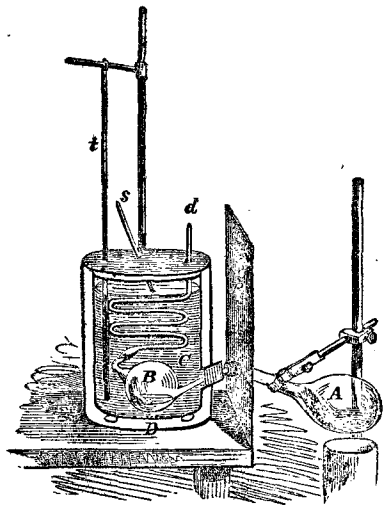
FIG. 140,



temperature of 10 litres 53°·6 C. It is found that a litre of water, if converted into steam of 100°, and condensed again into the liquid form, would raise about $5\frac{1}{2}$ litres of water from 0° to 100° C.

We owe to Andrews (*Q. J. Chem. Soc.* 1848, i. 27) a careful determination of the latent heat of a number of vapours: fig. 141 shows the mode of procedure which he adopted. The liquid to be tried is placed in the flask A, the neck of which has a very short bend, and is connected with a glass receiver, B, furnished with a spiral condensing-tube, terminating at *d*; this receiver is placed in a vessel C, with a considerable quantity of water, which has been accurately weighed. The liquid is distilled over into B: the quantity that condenses is carefully weighed, and the rise of temperature experienced by the water used for condensation is estimated by a very sensitive thermometer, *t*. The whole is enclosed in an outer tin-plate vessel furnished with a lid, which acts as a screen, and it is further protected from the radiation of the lamp by the tin-plate screen R; *s* is a light glass tube for agitating the water. The result obtained has, however, to be corrected by other experiments for the heat absorbed by the metallic parts of the apparatus, and for that which is lost by radiation during the time that the experiment lasts; allowance has also to be

FIG. 141.



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water, whilst the condenser, C C, is wrapped in flannel, and the apparatus is left to itself. As the water in A becomes cool, it re-dissolves the condensed ammoniacal gas which evaporates rapidly from the vessel, C, producing a great and sudden depression of temperature.

If air finds admission to the interior, the rapidity of congelation may be greatly reduced. In such a case it becomes necessary to get rid of the air, and it may be expelled in the following manner:—The temperature of the boiler having been raised to about 140° (60° C.), water having been placed in the cup, D, the screw at the bottom of the cup which communicates with the receiver is slightly relaxed; if air be present, the disengaged gas will carry a portion of the air with it, which will rise to the surface of the water, whilst the ammonia is dissolved: as soon as the escaping gas is wholly dissolved by the water, the screw must be closed firmly, and the distillation proceeded with as above directed.

M. Raoul Pictet, of Geneva, has employed liquid sulphurous anhydride, condensed by a pressure of two or three atmospheres, and allowed to volatilize in a vessel from which the gas is removed by a pump and returned to the condenser. As a circulating fluid, dilute glycerin is used instead of salt water.

Mr. King has recently contrived a machine in which, by means of the expansion of compressed air, he is enabled to produce an amount of cold equal to that generated by the ether machine for an equal consumption of coal. (Jas. Young.)

made for the heat which the condensed liquid has given out after its liquefaction, in cooling down from its boiling-point to the temperature of the water used in the condenser.

The results obtained in this delicate branch of inquiry by Despretz, and by Brix, which, however, embraced a much smaller number of liquids, agree pretty closely with each other and with the experiments of Andrews. These results, with some of those obtained by Favre and Silbermann, who also have made numerous experiments upon this subject (*Ann. Chim. Phys.* 1853 [3], xxxvii. 461), are given in the following table:—

Latent Heat of Vapours.

Substance.	Equal Masses ° C.	Equal Masses ° F.	Equal Masses Steam = 1000.	Equal Vols. Steam = 1000.	Observer.
Water	536·67	966·0	1000	1000	Regnault
" "	535·90	964·6	998·6		Andrews
Wood Spirit	263·70	474·7	491·4	873·5	"
" "	263·86	474·9	491·7	874·1	Favre and
Alcohol	208·92	376·1	389·3	994·8	Silbermann
" "	202·40	364·3	377·1	963·8	Andrews
Fusel Oil	121·37	218·5	226·1	1105·6	F. and S.
Formic Acid	120·72	217·3	224·9	574·8	"
Methyl Formiate ...	117·10	210·8	218·2	727·3	Andrews
Butyric Acid	114·67	206·4	213·7	1044·6	F. and S.
Methyl Acetate... ...	110·20	198·4	205·3	844·2	Andrews
Formic Ether	105·30	189·5	196·2	806·6	"
Valeric Acid	103·52	186·3	192·9	1093·1	F. and S.
Acetic Acid	101·91	183·4	189·9	633·0	"
Acetic Ether	105·80	190·4	197·1	963·8	"
" "	92·68	166·8	172·7	844·3	Andrews
Ether...	90·45	162·8	168·5	692·9	"
" "	91·11	164·0	169·8	697·9	F. and S.
Methyl Butyrate ...	87·33	157·2	162·7	922·1	"
Carbonic Disulphide...	86·67	156·0	161·5	681·9	Andrews
Oil of Lemons	70·02	126·0	130·5	985·8	F. and S.
" "	80·00	144·0	149·1	1126·3	Brix
Oil of Turpentin ...	74·00	133·2	137·9	1041·8	"
" "	68·73	123·7	128·1	967·6	F. and S.
Terebene	67·21	121·0	125·2	946·2	"
Oxalic Ether	72·72	131·0	135·5	1099·1	Andrews
Amylic Ether	69·40	124·9	129·3	1135·1	F. and S.
Cetylic Alcohol, Ethal	58·48	105·3	109·0	1465·0	"
Phosphorous Chloride	51·42	92·6	95·8	731·9	Andrews
Ethyl Iodide	46·87	84·4	87·3	756·9	"
Methyl Iodide	46·07	84·9	85·8	677·2	"
Bromine	45·60	82·1	85·0	755·3	"
Stannic Chloride ...	30·53	54·9	56·9	821·7	"
Iodine	23·95	43·1	44·6	629·7	F. and S.

The numbers which represent the latent heat of equal volumes of each vapour are obtained by multiplying the numbers in the fourth column by the molecular weight of each compound, divided

by 18, the number for the molecule of aqueous vapour, H_2O. The numbers contained in the second column indicate the quantities of water in grammes, the temperature of which would be raised 1° C. by condensation into the liquid form of a gramme of the vapours of each of the various liquids mentioned; the liquid condensed being supposed in each case to be at the temperature of its own boiling-point. For instance, the conversion of one gramme of steam at 100° C. into water at 100° would raise 536·67 grammes of water from 0° to 1° C. So the condensation of one gramme of the vapour of alcohol at 78°·4 into liquid alcohol at 78°·4 would heat 208·92 grammes of water from 0° to 1° C.

(187) The density of steam increases directly as its pressure. Watt concluded from his experiments that the same mass or quantity of steam, whatever its density may be, contains the same quantity of heat, its latent heat being increased in proportion as its sensible heat is diminished or absorbed. For instance—

A certain quantity of steam at 100° C. condensed at 0° C., gives out . .	100 units of sensible heat, and 536 „ of latent heat.	
Amounting together to	636	
The same quantity of steam at 121° C., condensed at 0°, gives out . . .	121 „	of sensible heat,
But only	515 „	of latent heat.
Still amounting together to	636	
The same quantity of steam at 34°, condensed at 0°, gives out . . .	34 „	of sensible heat.
But now as much as	602 „	of latent heat.
Making together, as before	636	

Regnault has, however, shown by a series of laborious experiments, that although the assumption of this rule may not lead to serious errors in practice, and although, consequently, there is but little saving of fuel in performing evaporations at a low temperature, yet that it is not strictly correct. It is true that the latent heat decreases as the sensible heat rises, but this diminution is less rapid than the rise in sensible heat; for, in reality, the sum of the latent and sensible heat increases as the temperatnre rises, by a constant quantity, equal for each degree to 0°·305 c: this may be seen in the subjoined table, in which it is assumed that the sensible heat of steam may be neglected for all degrees below zero Fahrenheit:—

Latent and Sensible Heat of Steam at different Temperatures.

Pressure in atmospheres.	Temperature. ° F.	Latent heat. ° F.	Sum of latent and sensible heat. ° F.
0·00146	0	1114	1114
0·00603	32	1091·7	1123·7
1·00000	212	966·0	1178·0
8·00000	339·5	877·3	1216·8

	° C.	° C.	° C.
0·006	0	606·5	606·3
1·000	100	537·0	637·0
2·000	120·8	522·8	643·6
8·000	170·8	488·0	658·8

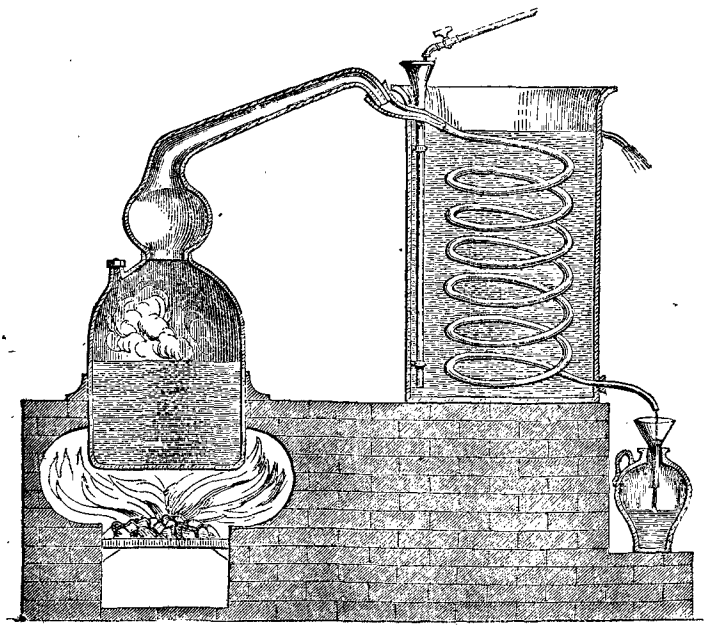
It must be borne in mind that equal volumes of different liquids produce very different volumes of vapour. Water furnishes a much larger volume than any other liquid, a cubic inch of water at 100° C. expanding to nearly a cubic foot of steam at 100°, or more accurately to 1694 times its volume. The following table shows the volume of vapour which is furnished by a cubic inch of four different liquids, at their respective boiling-points. Equal volumes of different vapours, taken at the boiling-points of their respective liquids, consequently possess very different densities, as is shown by the last column of the table :—

1 cubic inch of each liquid at 15° C. yields in the case of	Cubic inches of vapour at its boiling-point.	Boiling-point.		Weight in grains of 100 cubic in. of each vapour at its boiling-point.
		° C.	° F.	
Water	1694	100·0	212	14·92
Alcohol	498	78·4	173·1	40·47
Ether	247	35·6	95·6	74·14
Oil of Turpentin	225	161·0	321·8	96·84

(188) *Distillation.*—The rapid formation of vapour during ebullition is often made use of by the chemist for the purpose of separating liquids from solids,—as in the ordinary case of distilling water to free it from the impurities dissolved in it, or for the separation of two liquids which differ in volatility, as in procuring spirit of wine from a fermented liquor. In such operations the arrangements for condensation acquire considerable importance ; they are of various kinds, but the *worm-tub* is the apparatus most usually employed : it consists of a spiral pipe called a *worm*, which is

shown in fig. 142, surrounded by a considerable volume of cold water: the vapour passes from the boiler into the worm, is condensed, and runs off at the lower aperture into suitable receivers.

FIG. 142.

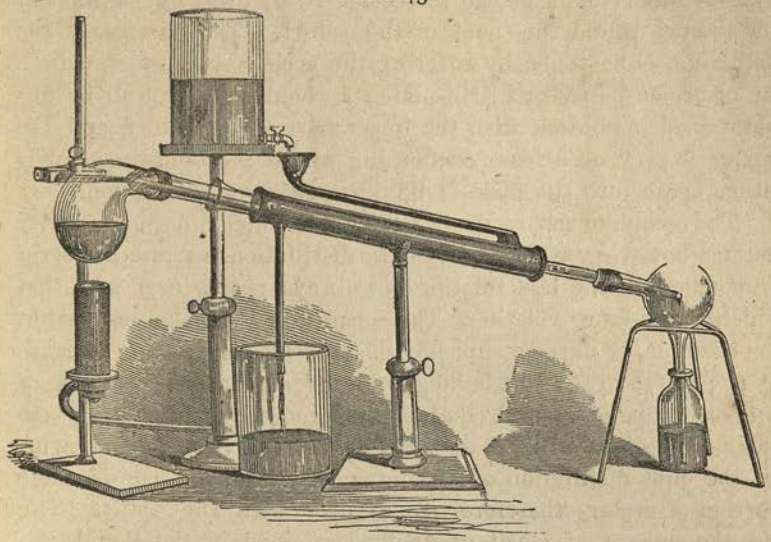


Fresh additions of cold water are continually required in the *refrigeratory*, as the worm and tub are called. The heat is greatest in the upper coils, where the hot vapour enters; and as the heated water, from its diminished density, remains at the top, it is necessary, in supplying the fresh water for cooling, to allow it to enter at the bottom of the vessel, while the heated portions flow off at the upper part. The object of giving to the steam-pipe an ascending direction, as it passes to the condenser, is to insure the return to the boiler of any particles of liquid which may have been mechanically carried up by the breaking of the bubbles in the act of ebullition.

Various modifications of condenser are employed in the laboratory. A convenient form of the apparatus is that known as Liebig's. It consists of an outer metallic tube, through the axis of which a glass tube is passed, and is supported by perforated corks: the space between the two tubes is filled with water, which is continually renewed by cold water supplied by a funnel near the lower extremity, while the hot water escapes at the other

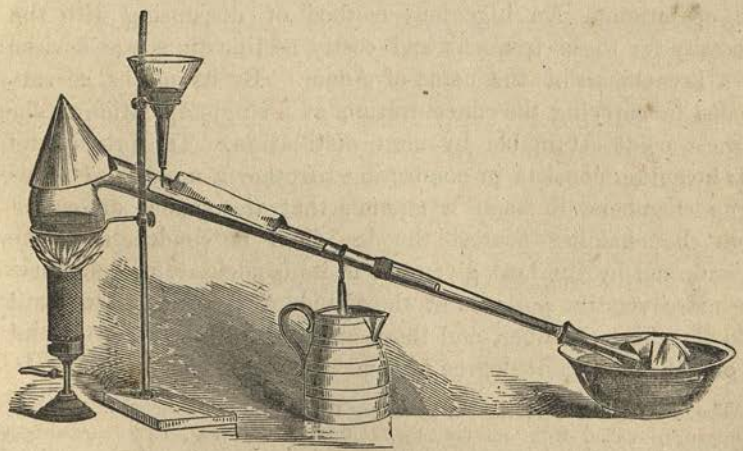
end. The method of using it is sufficiently indicated by the annexed figure.

Fig. 143.



When the products of distillation are not very volatile, it is often found convenient to make use of the evaporation of water from the neck of the retort as a means of condensation. Fig. 144

Fig. 144.



shows a method by which this can be effected, the neck of the retort being prolonged by the addition of the conical tube or *adapter*. Pieces of blotting-paper are used to distribute the water

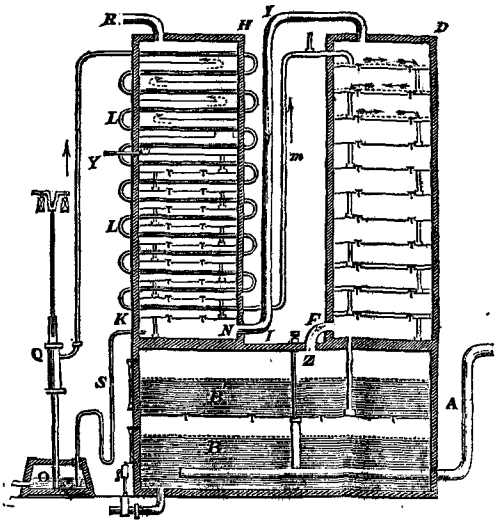
as it trickles slowly from the funnel, the throat of which is obstructed by a plug of tow: the superfluous water is carried off into a jug or other vessel placed to receive it, by means of a fillet of tow twisted round the neck of the retort. The progress of the distillation is hastened by covering the arch of the retort with a cap of brown paper or of tin-plate; a chamber of hot air is thus maintained in contact with the upper part of the retort, and the vapour is prevented from condensing where it would necessarily return again into the mass of liquid undergoing distillation.

The complete separation of two liquids which differ in volatility cannot, however, be effected by mere distillation, because a certain proportion of the less volatile one always passes over with that which is the more volatile. The separation of alcohol and water, for example, is never completely effected by distillation; because at 173°·1 (78°·4 C.) (the boiling-point of alcohol) the pressure of aqueous vapour is still considerable; indeed it is sufficient to balance a column of mercury nearly 13 inches (330$^{mm.}$) in height. In the first distillation of the fermented liquor, a considerable portion of water, therefore, comes over with the spirit. The less the amount of spirit originally contained in the liquid, the larger is the portion of water in the distilled liquor. By a second distillation the portion of water in the distillate is reduced; and the process may be repeated with like effect until the reduction of the portion of water in each successive product of distillation no longer compensates for the waste and expense of the operation. An ingenious method of dispensing with the necessity for these frequent and costly rectifications was devised by a Frenchman of the name of Adam. By its means he succeeded in carrying the concentration at a single operation to the highest point attainable by mere distillation. The principle of this invention consists in connecting together a number of rectifying chambers, in such a manner that the vapour driven off from the chamber nearest the fire shall be condensed in the second, and by the heat given out in its condensation shall cause the more volatile portions of the liquid of the second to distil into the third chamber, and those of the third into a fourth, and so on till a sufficient degree of concentration is effected.

The most effective method of attaining this object is exhibited in the form of apparatus called from its inventor, *Coffey's still*. Fig. 145 represents a section of one of these stills. B B′ is the body of the still, which is made of copper, and enclosed in a case of wood, to prevent loss of heat: upon the body two columns, D F, H K, are supported; O is the vessel from which the liquor for distillation is raised by the pump Q; the liquor enters the column H K, by the long spiral pipe L L, by which it is ultimately conveyed, through the pipe *m* to

the top of the column D F. The heat employed in the distillation is not the direct heat of a fire, but is procured by injecting steam obtained from a boiler not shown in the figure. The steam enters the body of the still through the pipe A; the amount of steam admitted being regulated by a valve, the handle of which is shown at F. B B′ is divided into two chambers by means of a copper shelf, pierced with numerous small holes, which allow the passage of steam upwards, though they are sufficiently small to prevent the descent of any considerable quantity of liquid which may be resting upon the shelf. The steam is at first condensed in the cold liquid of the lower chamber, but it quickly raises this liquid to the boiling-point, driving off the alcoholic portions first, as they are the most volatile.

FIG. 145.



This vapour traverses the liquid which rests in B′, on the perforated shelf, and gradually raises it to the boiling-point, driving off from it the alcohol in vapour; this vapour passes off by a pipe Z, to the bottom of the column D F. This column is divided into a series of compartments, by perforated shelves of copper; each of these shelves is provided with a pipe for carrying off the liquid to the shelf below. This pipe is long enough to dip below the surface of the liquid on the shelf beneath it, and projects about an inch above the upper surface of the shelf to which it is attached; a stratum of liquid about an inch in depth is thus retained upon each shelf, and is traversed by the vapours which ascend from the shelf next below it. The *wash* or liquid for distillation, having become heated during its passage through the spiral pipe in the column H K, falls upon the uppermost perforated shelf in D F, flows off at the farthest end of that shelf, and then falls upon the next shelf; thence it passes to the third, and so on in succession to each shelf: as it descends, it encounters the ascending vapours, which at each successive step of the ascent become more and more alcoholic—the wash, as it descends becoming weaker and weaker, until when it reaches the vessel B B′, it is wholly deprived of spirit. If the quantity of the ascending vapour should become at any time too great to pass through the perforations in the shelves, the pressure opens the valves T T, which are provided for security in each shelf. The vapour having reached the top of the column D F, is conveyed by the steam-pipe I I N, to the bottom of the finishing column or rectifier H K. The lower part of this column, as high as the pipe Y, is constructed exactly upon the same plan as the column D F, but in each compartment between the shelves the spiral pipe L L makes three or four convolutions, and thus becomes warmed by the ascending heated vapours. In this second column the spirituous liquid distilled over from the first column undergoes a successive rectification upon each of the lower shelves, and becomes more and more concentrated by the ascent of the alcoholic vapours, which, by

their condensation at each successive stage, emit sufficient of the heat previously held latent to effect the distillation of the more volatile portions of the liquid by which they are condensed. The five upper shelves of this column merely act as a condenser for the alcoholic vapours; these shelves are not perforated, and are attached to the alternate sides of the column, leaving a narrow passage at one end of each shelf, so as to oblige the vapours to describe a zigzag direction: the pipe T carries off the finished spirit into proper receivers; the pipe R carries off any uncondensed spirituous vapour to a refrigeratory, whilst the weak spirit which reaches the lower part of the column is returned by the pipe S to the vessel O. The spent wash, as it accumulates in B B', is drawn off at intervals, and the still can thus continue its operations without intermission.

In chemical investigation recourse is frequently had to fractional distillation for the partial separation of liquids of different volatilities. When a retort is employed a thermometer is adapted by a cork to the tubulure, the bulb being placed above the liquid, but below the lower edge of the neck of the retort. Unless there is a considerable difference between the volatilities of the bodies an incomplete separation is effected, much of the less volatile bodies passing over with those of lower boiling-points. The separation is made much more complete by changing the form of apparatus, imitating, in fact, on a small scale, the action of Coffey's still. For this purpose a flask may be employed, to the neck of which is adapted a glass tube of about a half or three quarters of an inch in diameter, on which five or six bulbs have been blown, and which is surmounted by a small glass alembic head. A thermometer is placed in the tubulure of the alembic head, and another thermometer may be inserted through a side tube into the lowest bulb. When the distillation is carried on slowly the vapour of the most volatile body passes over first, those of lower boiling-point condensing on the bulbs, and flowing back into the flask. The contractions between the bulbs check the diffusion of the different vapours, and the more volatile liquid is being continually carried upwards from the condensed liquid in the bulbs by the rising vapours. When the two thermometers indicate the same temperature a homogeneous liquid is passing over; a rise of the lower one indicates that a second vapour is commencing its passage. Several more complex forms of this apparatus have been devised.

(189) *Evaporation.*—All liquids, at temperatures far below their points of ebullition, emit vapour by the tranquil process of evaporation. The amount of vapour given off at a constant temperature differs greatly in different liquids, and is dependent upon the temperature at which each liquid boils.

The great difference in the volatility of liquids at the same temperature is strikingly shown by filling a number of barometer-tubes (fig. 146) with mercury,

and inverting them in a bath of the same metal. One of these tubes (1) may be kept as a standard of reference: if into one of the others (2) a few drops of water be allowed to ascend, an immediate depression of the column of mercury

FIG. 146.

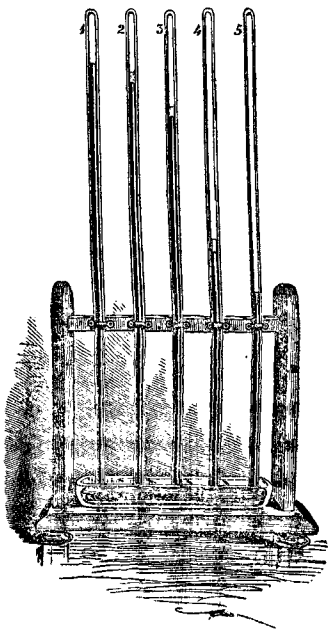
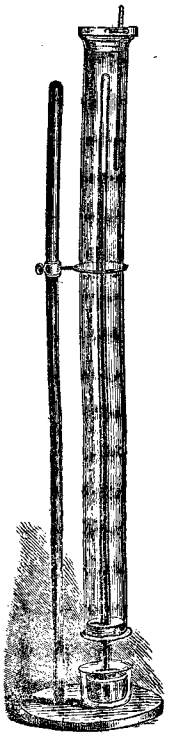


FIG. 147.



is observed, due to the elasticity of the aqueous vapour furnished by the evaporation of the water. If into a third tube (3) alcohol be introduced, a greater depression will be perceptible; carbonic disulphide in a fourth tube (4) will produce a still greater depression, and if ether be admitted to a fifth (5), the height of the mercurial column will be still less. Now let a second wider tube, closed below by a cork, be placed round the exterior of any one of these tubes, so as to inclose nearly its whole length, as in fig. 147: let the outer case thus formed be filled with water, the temperature of which is gradually raised, so as to communicate the heat uniformly to the tube within. A progressive depression of the mercurial column is thus produced; and by measuring the amount of this depression, it is found that the pressure of the vapour emitted from each liquid increases as the temperature rises, until at the boiling-point of the liquid the pressure becomes equal to that of the air.

If the temperature increase according to the terms of an arithmetic ratio, the pressure rises according to the terms of a geometric progression, the ratio of which differs for each liquid.

The following table comprises some of the results of Regnault's

experiments upon the pressure of the vapours of various liquids at equal temperatures. The pressure of the vapour is measured by the height of a column of mercury in millimetres which each vapour will support at the temperatures quoted. That of water is taken from Regnault's *Relations des Expériences*, &c. (*Mem. de l'Institut*, 1847, xxi. 624), and those of the other liquids the temperatures of which were determined by a mercurial thermometer from the *Comptes Rendus*, 1860, l. 1063:—

Temp. ° C.	Ether.	Carbonic Disulph.	Chloroform.	Alcohol.	Water.	Oil of Turpentin.	Temp. ° F.
−20	67·49	43·48		3·34	·927		− 4
−10	113·35	81·01		6·58	2·093		+14
0	183·34	131·98		12·83	4·600	2·07	32
+10	286·40	203·00		24·30	9·165	2·94	50
20	433·26	301·78	160·47	44·48	17·391	4·45	68
30	636·33	436·97	245 91	78·49	31·548	6·87	86
40	909·59	616·99	366·20	133·64	54·906	10·80	104
50	1271·12	856·71	530·96	219·88	91·982	16 98	122
60	1728·52	1163·73	751·01	350·26	148·791	26·46	140
70	2307 81	1551·84	1038·09	541·21	233·093	40·64	158
80	3024·41	2033·77	1404·57	812·76	354·643	61·30	176
90	3898·05	2622·23	1863·12	1188·43	525·450	90·61	194
100	4950 81	3329·54	2426 52	1694·92	760·00	131·11	212
110	6208 37	4167·18	3106 83	2361·63	1075·37	185·62	230
120	7702 20	5145·43	3916·17	3219·68	1491·28	257·21	248
130		6273·03	4865·65	4301·04	2030·28	348·98	266
140		7556·88	5965·76	5637·00	2717·63	464·02	284
150			7226·49	7258 73	3581·23	605·20	302
160			8657·72		4651·62	775 09	320
170					5961·66	975·42	338
180					7546·39	1207·92	356
190					9442·70	1473·24	374
200					11688·96	1771·47	392

(190) *Dalton's Law of Pressure of Vapours.*—It was assumed by Dalton that the pressure of all vapours was equal, if compared at temperatures which represented differences of an equal number of degrees above or below the boiling-points of their respective liquids, the pressure of the vapour increasing according to the terms of a geometric progression uniform for all liquids, as the temperature rose in terms of an arithmetic progression. This law is not strictly in accordance with the results of experiment. However, for short distances above and below the boiling-point, it is very nearly true, excepting in the case of mercury, and may be employed for the purpose of correcting the observations of the boiling-points of liquids made at atmospheric pressures which are but little above or below the standard pressure of 760^{mm}.

The following table exhibits the pressure of the vapours of five different liquids at corresponding distances above and below their boiling-points.

Pressure of Vapours at equal distances from the Boiling-Points of the Liquids.

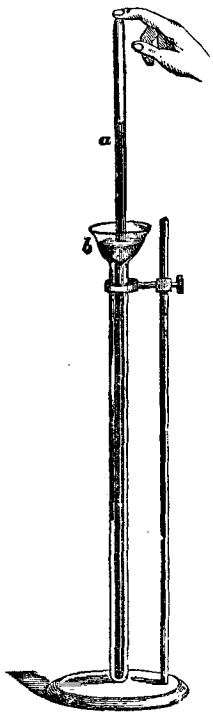
Number of degrees F. above or below boiling.	Regnault. Water.		Ure. Alcohol. Sp. Gr. 0·813.		Ure. Ether.		Marx. Carbon. Disulph.		Avogadro. Mercury.	
	Temp. ° F.	Press. Inches.	Temp. ° F.	Press. Inches.	Temp. ° F.	Press. Inches.	Temp. ° F.	Press. Inches.	Temp. ° F.	Press. Inches.
+ 40	252	63·14								
+ 30	242	52·90			134	50·9				
+ 20	232	44·06			124	42·64	137	42·19		
+ 10	222	36·47	183	37·00	114	35·2	127	35·60		
Boiling-Point	212	30·00	173	30·00	104	30·00	117	29·87	680	30·00
— 10	202	24·50	163	24·20	94	24·70	107	24·91		
— 20	192	19·87	153	19·30	84	20·00	97	20·65		
— 30	182	16·00	143	15·05	74	16·10	87	17·00		
— 40	172	12·78	133	11·60	64	13·00	77	13·89		
— 50	162	10·12	123	8·75	54	10·30	67	11·27	630	19·85
— 60	152	7·94	113	6·70	44	8·10	57	9·07		
— 70	142	6·18	103	4·90	34	6·20	47	7·24		
— 80	132	4·76	93	3·67			37	5·73		
— 90	122	3·63	83	2·73			27	4·49	590	8

The ether used in these experiments could not have been perfectly pure, as its boiling-point is too high. The boiling-point of mercury was estimated by a mercurial thermometer without correction for the increasing rate of expansion at high temperatures.

The increase of pressure produced by heat in those vapours which are in contact with the liquids by which they are furnished, indicates also a corresponding increase in their density: the one may, in fact, be calculated from the other. When the temperature is reduced, the pressure falls, and a portion of the vapour is condensed. There is, indeed, for every vapour a maximum density for each temperature, which, when the liquid is in contact with the vapour, is speedily attained, but which cannot be surpassed, no matter how much the pressure to which the vapour is subjected may vary; an increase of pressure immediately condenses a part of the liquid that had evaporated, and a diminution of pressure is attended with immediate volatilization of a fresh portion of the liquid: consequently a cubic centimetre of vapour of any particular liquid at any given temperature, is always of the same pressure, and possesses the same density.

If a small quantity of ether be thrown up into the vacuum of the barometer tube, represented in fig. 148, the length of the column of mercury, *a b*, above the level of that in the bath, will continue to be nearly the same whether the tube be raised or lowered in the outer vessel. If it be raised, fresh ether will evaporate; if depressed, part of the vapour will be condensed.

FIG. 148.



(191) *Limit of Evaporation.*—From what has just been stated it might be supposed that all liquids, even at the lowest temperature, were constantly emitting vapour. That mercury does so at common atmospheric temperatures may be shown by a very simple experiment. Place at the bottom of a bottle a few drops of mercury, and suspend in the neck a bit of gold leaf; in a few weeks the lower portions of the gold will become white from the condensation of the vapour of mercury upon it. In the tube of a well-made barometer the same thing is shown by the formation of a dew of metallic globules in the space above the column of metal. Faraday has, however, proved that there is a temperature below which this volatilization ceases, a temperature which varies for different substances; for mercury the limit is about 4° C.: for sulphuric acid the limit is much higher, since the acid undergoes no sensible evaporation at ordinary atmospheric temperatures. The cohesion of the liquid here appears to overcome the feeble tendency to evaporation.

It is not necessary for the evaporation of a body that it should be in the liquid form. Solid camphor is constantly emitting vapour, which condenses in a crystalline form on the sides and upper part of the vessel which contains it. Ice, if introduced into the vacuum of a barometer, immediately causes a depression of the mercurial column amounting at 0° C. to upwards of $0{\cdot}457^{mm.}$, and even at 0° F. the pressure of the vapour of ice is found to amount to $0{\cdot}1^{mm.}$ It is owing to this evaporation that patches of snow and tufts of ice are observed gradually to disappear even during the continuance of a severe frost.

Regnault found in his experiments that no appreciable change in the curve which represents the pressure of a vapour is produced by the passage of a body from the solid to the liquid state;

that is to say, that there is no abrupt diminution in the amount of vapour emitted from a body when it becomes solid.

It has been shown that if the temperature of one of the tubes, shown in fig. 145, which contains a volatile liquid, be uniformly raised throughout its entire length, the pressure of the vapour increases rapidly till the liquid reaches its boiling-point. The application of heat to one portion only of the tube, however, is attended with a very different result: the liquid may even be heated to ebullition, and it will distil and be condensed, but unless the whole of that portion of the tube which is filled with vapour he heated to the same degree, no corresponding increase of pressure will be observed: the pressure can never exceed that of the vapour which would be emitted if the liquid were at the same temperature as that of the coolest portion of the tube above the liquid; because the excess of vapour is at once condensed as soon as it reaches this colder part of the space. The ether, for example, in the barometer-tube 5, fig. 147, may be made to boil by the heat of the hand, but the height of the column of mercury undergoes little change; the ether vapour being condensed in the colder portions of the space as rapidly as it is produced.*

(192) *Circumstances which Influence Evaporation.*—In the process of evaporation, the vapour is supplied only from the superficial layer of the liquid. It is therefore evident that the extent of surface exposed must greatly influence the amount and rapidity of evaporation independently of the temperature. Now if the evaporating surface be in any way protected, as by allowing a small quantity of oil to become diffused over it, evaporation is entirely suspended. Advantage is sometimes taken of this fact in the laboratory in cases where it is necessary to maintain a gentle heat for many hours: the vessel to be heated is supported in a larger one containing water, upon the top of which a little oil has been poured; under these circumstances the danger of the water-bath becoming dry is obviated, and the temperature required is kept up by a smaller expenditure of fuel, because the escape of latent heat by evaporation is prevented. When, on the contrary, a rapid evaporation is necessary, a large extent of surface must be exposed. In the salt works of Cheshire, for instance, the brine is evaporated in shallow pans, 4 or 5 feet (1·2 or 1·5 metre) wide and 40 or 50 feet (12 or 15 metres) in length, the fire being lighted

* In the Appendix will be found a Table giving the pressure of aqueous vapour for each degree C. between 0° and 100°.

at one end and the flue passing horizontally underneath to the other extremity. At Salzburg, in the Tyrol, the same object is effected by pumping the weak brine into reservoirs, whence it is allowed to trickle down through stacks of brushwood, by which means the surface exposed to evaporation in the air is almost indefinitely increased. In the southern parts of Europe the sea-water is admitted into extensive shallow pans excavated on the sea-coast, where by exposure to the sun's rays it becomes concentrated, and the salt crystallizes out.

Another circumstance which influences the rate of evaporation is the pressure upon the surface of the liquid. Upon this subject a series of experiments was made by Daniell (*Quart. Journ. Sci.* 1834, xvii. 46). Under a receiver connected with the air-pump, he placed a circular dish of water, 2·7 inches in diameter, and supported it above a dish containing concentrated sulphuric acid,—the object of using the acid being to absorb the aqueous vapour as fast as it was generated: the results of these experiments are given in the following table:—

Rate of Evaporation under different Pressures.

Pressure in Inches of Mercury.	Grains Evaporated.	Pressure in Inches of Mercury.	Grains Evaporated.
30·4	1·24	1·9	15·92
15·2	2·97	0·95	29·33
7·6	5·68	0·47	50·74
3·8	9·12	0·07	112·32

The time in each experiment was 30 minutes, the temperature 45° (7°·2 C.). It is obvious that the rapidity of evaporation under these circumstances was inversely as the pressure, which was read off upon the gauge.

The resistance offered by the pressure of a gas or vapour upon the surface of a liquid is purely mechanical; and it follows as a consequence of the law of the diffusion of gases, that the quantity of vapour which rises from a volatile body in a confined space, is the same whether that space be filled with air or not.* The time that is occupied before the space shall have received its full

* Regnault finds that this is not absolutely true,—the pressure of aqueous vapour in air being slightly less than *in vacuo*, but the difference does not amount to more than 2 per cent. at its maximum. The same thing was found to hold good with the vapour of ether, the pressure of which, whether in air, in hydrogen, or in carbonic anhydride, was always lower than it was at the same temperature *in vacuo*.

complement of any given vapour varies inversely with the pressure; and with different vapours under similar pressures, the time varies with the diffusiveness of the vapour. The vapour, as it rises, adds its own pressure to that of the air present. When a liquid evaporates into an empty space, the pressure due to the temperature and, consequently, the maximum density of the vapour, is acquired at once; but when it evaporates into a gas, that degree of density is not acquired until after the lapse of a variable interval of time. The circumstance which in both cases finally limits the evaporation of the liquid, is the pressure of its own vapour upon its surface. It is therefore clear that the larger the proportion of moisture that is contained in the air at any given time, the smaller will be the quantity of aqueous vapour that rises from an exposed surface in a given time; and that in proportion as the space is more nearly charged with vapour, the more slowly is each succeeding portion of vapour produced. Evaporation, in short, is more rapid in a dry than in a moist atmosphere. For the same reason, evaporation proceeds more rapidly during a breeze than when the air is still: for the air which rests on the surface of a liquid soon becomes charged to the maximum with vapour, and then all further evaporation would cease were it not for circulating movements, which, even in the stillest air, are occasioned by the change of density due to the accession of moisture; the currents produced by a breeze assist these movements, and the vapour rises into portions of air which are being continually changed, so that the pressure of the aqueous vapour on the surface of the liquid is rapidly removed.

In the case of mixed liquids, Gay-Lussac inferred from his experiments that the pressure of the mixed vapour was equal to the sum of the pressures of the two vapours taken separately. This, however, is true only for liquids which, like carbonic disulphide and water, or like benzol and water, do not sensibly dissolve each other; in other cases, as the experiments of Regnault and of Magnus have shown, the pressure may scarcely exceed that of the more volatile liquid;—for example, in the case of a mixture of ether and water, the pressure is scarcely higher than that due to ether only. If the two liquids be soluble in each other in all proportions, as water and alcohol, the pressure of the mixed vapour is generally greater than that of the less volatile, but less than that of the more volatile liquid.

Wüllner (*Pogg. Annal.* 1860, cx. 564) has shown that the pressure of aqueous vapour emitted from a saline solution, when

compared with that of pure water, is diminished by an amount proportional to the quantity of anhydrous salt dissolved, when the salt crystallizes in the anhydrous form, or when it furnishes efflorescent crystals. In cases where the salt is deliquescent, or has a powerful attraction for water, the reduction of pressure is proportional to the percentage of the crystallized salt. For example, sulphates of sodium, nickel and copper, nitrate of calcium, and ordinary or hydric disodic phosphate (Na_2HPO_4) produce a diminution of pressure proportional to the percentage of the anhydrous salt, whilst for caustic potash and soda, and for calcic chloride, it is proportional to the hydrates KHO, 2 H_2O; 2 NaHO, 3 H_2O; $CaCl_2$, 3 H_2O. The amount by which the pressure is reduced for equal quantities of the compounds compared, varies greatly with their nature. Sulphate of nickel, for instance, dissolved in the proportion of 10 per cent. ($NiSO_4$) reduces the pressure of the vapour at 100° C. by $13^{\cdot mm\cdot}2$, whilst a similar proportion of potassic hydrate (KHO) effects a reduction of $35^{\cdot mm\cdot}6$.

Evaporation in a confined space, in which the atmosphere is kept constantly in a state of dryness, is often resorted to in the laboratory. Crystallizations on a small scale are frequently effected in this way: the liquid evaporates, and is absorbed by a surface of sulphuric acid, as in the experiment of Leslie (185). The evaporation may be rendered quicker or slower according to the extent to which the exhaustion of the receiver is carried. Many compounds which would be injured by exposure to air, or to a moderate rise of temperature, may be dried effectually in this manner.

As a necessary consequence of the evaporation which is continually going on over the entire surface of the earth, the atmosphere is at all times charged with moisture, the percentage of which is perpetually varying, but it is almost always below that which experiment gives as the maximum density for aqueous vapour due to the observed temperature. It is owing to the circumstance that the air is rarely fully charged with vapour, that wet bodies become dry, and that the surface of the soil, although saturated with moisture, yet in a few hours or days becomes parched and dusty. By the process of evaporation from the surface of the land as well as of the ocean, a natural distillation is thus continually effected, by which a perpetual circulation of water is maintained; the waters conveyed by the rivers into the sea return imperceptibly into the atmosphere. The vapour thus raised either assumes an invisible form, or it floats about in masses of cloud; these are at length arrested, particularly by mountains

and elevated ridges of land, and becoming condensed, descend as showers, and supply stores of water, which flow down the sides of the hills, and collect in the ravines, or else are absorbed into the porous strata. The waters thus absorbed sink into the soil until they meet with a bed of clay or some other stratum impervious to moisture; by this they are arrested, and flow along its surface till they burst out as springs in the valleys. These springs in their turn furnish constant supplies to the rivers, and the rivers, after irrigating the countries through which they flow, again empty themselves into the ocean. The frequency of rain, and various other meteorological phenomena of the highest interest and importance,—in fact, many of the great peculiarities of climate,—are mainly influenced by the variations in the percentage of moisture which is contained in the atmosphere. The knowledge of the quantity of aqueous vapour which exists at any given time in a certain volume of air, becomes, therefore, a problem which is constantly requiring solution for meteorological purposes. Instruments employed for this purpose are termed *hygrometers* (from ὑγρὸς, moist, and μέτρον, a measure). Various methods have been proposed for determining the percentage of moisture in the air; the simplest and the most accurate of these consists in the determination of the *dew-point*.

(193) *Dew-point*.—It is evident that a reduction of temperature in a space already charged to the maximum with vapour, must produce a deposit of moisture in the liquid form. Such a result, in fact, accords with daily observation: for example, when a glass of cold water is brought into a warm and moist room, its surface becomes bedewed with moisture. This observation has been ingeniously turned to account for the purpose of determining the quantity of moisture present in the air at any given time. If the cold liquid be poured from one vessel to another, its temperature will be gradually raised; the quantity of dew which is formed on the outside of the vessel into which it is poured will become less and less, until it ceases to be formed at all. By noting with a sensitive thermometer the exact temperature at which this formation of dew ceases, the pressure of the aqueous vapour present in the air at that period can be readily ascertained from tables constructed for that purpose, and the corresponding percentage of moisture calculated. If the temperature of the air at the time be noted, it is easy to determine the additional percentage of moisture which the air at that time is capable of taking up. This comparison is generally made by calling the quantity of invisible vapour which it is possible for air to retain at the particular tem-

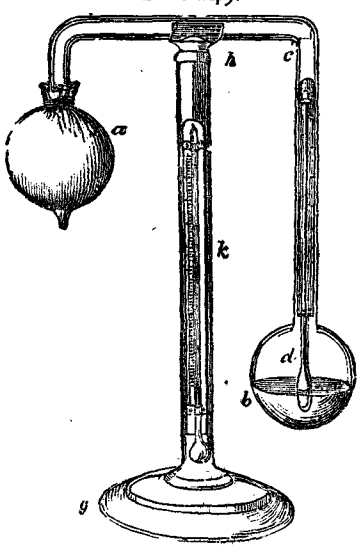
perature at the time of observation 1000, and calculating from the observed dew point the ratio which the amount actually present bears to that which might exist at that temperature. Suppose, for example, when the air is at 15° C., that the *dew-point* be as low as 10°; that is, the temperature at which dew begins to be formed is 10°. On reference to the table, it appears that the pressure of vapour at 15° amounts to $12^{\cdot mm}\cdot 699$ of mercury, while at 10° it is equal to only $9^{\cdot mm}\cdot 165$. Now the quantity of vapour is directly proportioned to its pressure; therefore, by proportion:—

$$12\cdot 699 : 9\cdot 165 :: 1000 : x \quad (=722).$$

722 represents the degree of atmospheric saturation at the time of observation.

Practically, however, it is desirable also to know the actual rate of evaporation at the time (or the number of grammes of water which evaporate from a given surface, such as a square metre of water freely exposed to the air), since it is this which in great measure determines the drying influence of the atmosphere upon the human body, and upon the substances exposed to its action.

FIG. 149.

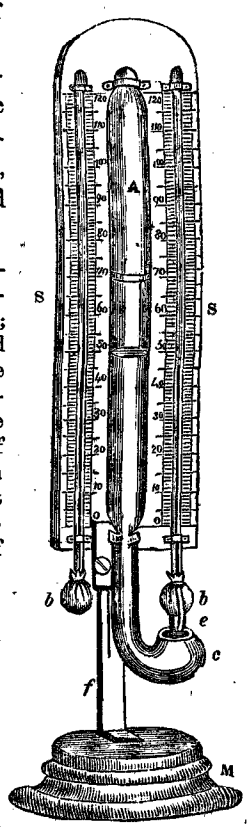


(194) *Daniell's Hygrometer.*—The method of observing the dew-point above mentioned, although it affords very exact results, is tedious in practice. To facilitate this operation, a beautiful instrument was contrived by Daniell, and termed by him the *Dew-point Hygrometer*. It consists essentially of a small cryophorus (fig. 149) containing ether instead of water, one limb of which, *c*, is longer than the other, and terminates in a ball, *b*, make of black glass, for the purpose of rendering the moment at which the deposition of dew occurs more readily observable. In the long limb of the instrument is placed a sensitive thermometer, *d*, the bulb of which is partially immersed in the ether. The second bulb, *a*, is covered with muslin. In constructing the apparatus, the ether is boiled to expel the air, and the instrument is hermetically sealed whilst the ether is still boiling. When the hygrometer is to be used, all the ether is driven into *b*, by inverting the instrument, and warming the bulb *a* with the hand; the instrument is then placed in the clip *h*, on the top of the stand *g*. On allowing a few drops of ether to fall on the muslin, the vapour within the ball *a* is condensed by the reduction of temperature occasioned by the rapid evaporation thus produced on its outer surface: fresh vapour rises from the surface of the ether in the blackened ball, owing to the diminished pres-

sure of the vapour above it: the temperature of this ether and of the ball in contact with it is lowered, and deposition of dew commences on the surface of the black ball, in the form of a ring, which coincides with the level of the ether. The moment that this occurs, the temperature marked by the included thermometer, *d*, is observed. It is, however, possible, if the reduction of temperature has been rapid, that the loss of heat may not be perfectly uniform throughout the ether in the black bulb, in consequence of which the temperature indicated by the thermometer, *d*, may be a little too high; it is therefore well to observe the temperature of *d* a second time, at the moment when the ring of dew disappears, during the return of the instrument towards the temperature of the surrounding air. This observation will now probably be slightly too low, but the mean of the two will accurately furnish the temperature of the dew-point. The temperature of the atmosphere at the time is indicated by the thermometer *k*.

In making an observation, the hygrometer should be placed at an open window, and a small cardboard screen should be interposed between the two bulbs, to prevent the vapour of the ether from extending to the atmosphere around the blackened bulb. With proper care, the instrument will yield results of great accuracy. An excellent hygrometer, on a similar principle, but of less portable construction, has been used by Regnault.

FIG. 150.



(195) *Wet-bulb Hygrometer.*—Other methods have been proposed for determining the quantity of moisture present in the atmosphere. Of these hygrometers, one only, the *wet-bulb hygrometer*, need be noticed here: it is shown in fig. 150.

In simplicity of action it leaves nothing to be desired, as it consists merely of two similar thermometers, S, S, placed side by side on the same stand, M *f*; the bulbs, *b*, *b*, of both are covered with muslin, and one of them is kept constantly moist by means of the capillary action of a few fibres of cotton, *e*, which connect it with a small vessel, A *c*, containing water. The rate of evaporation, and consequently the depression of temperature of the moistened bulb, will be greater in proportion as the atmosphere is further from its point of saturation; and tables have been given for determining the degree of saturation for all differences of temperature within the ordinary atmospheric range.

The elaborate researches of Regnault (*Ann. Chim. Phys.* 1845 [3], XV, 201) have shown that the indications of this hygrometer require a variety of corrections which cannot be correctly estimated. The formula which on the whole corresponds best with observation is that of Apjohn: $f' = f - \frac{d}{88} \times \frac{p}{30}$. In this formula f' is the pressure of steam at the dew-point, f is the pressure of steam at the observed temperature of the air, d is the difference in temperature of the two

thermometers, 88 is a constant coefficient for the specific heats of air and steam, p is the observed height of the barometer, 30 is the mean height of the barometer in English inches.

From an extensive series of comparisons made at the Greenwich Observatory between the wet-bulb hygrometer and Daniell's instrument, Glaisher concludes that the dew-point may be ascertained by multiplying the difference between the temperature of the dry and the wet-bulb by a number depending upon the temperature of the air at the time of observation, and subtracting the product from this last-mentioned temperature.

The numbers which he gives are contained in the following Table*:—

Dry Bulb. Temperature ° F.	Multiplier.	Dry Bulb. Temperature ° F.	Multiplier.
below 24	8·6	34 to 35	2·6
24 to 25	7·3	35 to 40	2·5
25 to 26	6·4	40 to 45	2·3
26 to 27	6·1	45 to 50	2·1
27 to 28	5·9	50 to 55	2·0
28 to 29	5·7	55 to 60	1·8
29 to 30	5·0	60 to 65	1·8
30 to 31	4·6	65 to 70	1·7
31 to 32	3·6	70 to 75	1·5
32 to 33	3·1	75 to 80	1·5
33 to 34	2·8	80 to 85	1·0

Since the pressure of aqueous vapour diminishes according to the terms of a *geometric* progression, whilst the temperature falls in *arithmetic* progression, the pressure of the vapour contained in the atmosphere at any given time is reduced by a fall of temperature more rapidly than in direct proportion to the fall; it therefore necessarily happens, that if a current of heated air, saturated with aqueous vapour, meet a current of cold air, also saturated with vapour, the intermingled portions of air at the mean temperature of the two can only retain a part of the vapour in the invisible condition, and the formation of a cloud or mist is the consequence. For example, suppose two equal volumes of air, one at 16° C. and the other at 4°, each saturated with vapour,

* When the dew-point was calculated by Apjohn's formula from the indications of the wet-bulb thermometer, the extreme differences from the true dew-point, furnished by Daniell's instrument, were found in two years at Greenwich to be −3°·9 between 65° and 70°, and +3°·6 between 75° and 80°; whilst the extreme differences by Glaisher's factors are −3°·7 between 75° and 80°, and +5°·6 between 75° and 80°.—(Daniell's *Meteorology*, ii. 100. See also Noble, *Proceed. Roy. Soc.* 1855, vii. 528.)

to be intermingled—the temperature of the intermingled air would be 10°. Now the pressure of aqueous vapour at 16° is $13^{\cdot mm\cdot}536$; at 4° it is $6^{\cdot mm\cdot}097$. The mean of these quantities is $9^{\cdot mm\cdot}816$, but the actual pressure of vapour at 10° is only $9^{\cdot mm\cdot}165$; consequently an amount of vapour represented by a pressure of $9^{\cdot mm\cdot}816 - 9^{\cdot mm\cdot}165$, or $0^{\cdot mm\cdot}651$, will be precipitated in the form of a cloud. It was upon this principle that Hutton accounted for the formation of rain, and so far as it goes, the theory is satisfactory: there are, however, other important causes concerned, but the subject cannot be appropriately discussed further in this work.

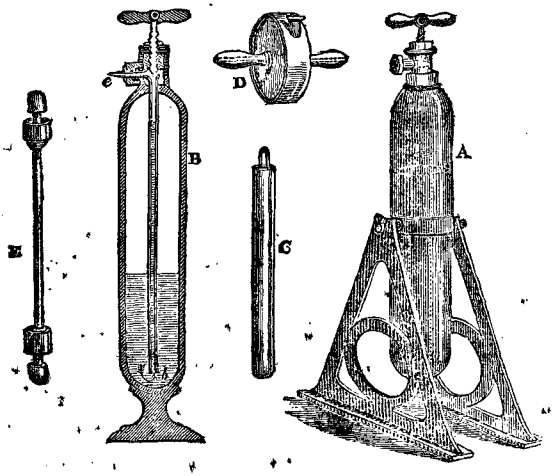
(196) *Liquefaction and Solidification of Gases.*—Vapours were formerly considered to be essentially different in their nature from gases; but numerous experiments, particularly those by Faraday (*Phil. Trans.* 1823, 160, 189, and 1845, 155), and Andrews (*Phil. Trans.* 1869, 575), have shown that the difference between gases and vapours is merely one of degree. Under Faraday's skilful manipulation, numerous gases have been reduced to the liquid state, and not a few have even been obtained in the form of solids. Some few of the gases have still resisted the best devised attempts to liquefy them; but it can hardly be doubted that all gases may be regarded as the vapours of liquids of an extremely high degree of volatility; the liquids resulting from the condensation of gases boiling at temperatures far below the ordinary atmospheric range: vapours, on the contrary, may be considered as the gases of liquids of comparatively low volatility.

Some of the gases are liquefiable with much greater facility than others; for instance, a mere reduction of the temperature to 4° (−20° C.) suffices to reduce sulphurous anhydride at the ordinary atmospheric pressure to the liquid form. Many gases, if generated in strong tubes, under the pressure of their own particles, lose their gaseous state. In this way carbonic anhydride, cyanogen, and several others, have been liquefied. But in other cases, a combination of the pressure obtained by means of a condensing syringe, with the application of a very low temperature, has been requisite. A convenient form of apparatus for this purpose has been devised by Andrews, who has succeeded in reducing the non-condensible gases in fine glass tubes, by pressure alone, to less than $\frac{1}{400}$ of the volume which they occupy under the ordinary conditions of the atmosphere, and in exposing them, still under this pressure, to a cold of from −77° to −101° C.

Carbonic anhydride may be manufactured in large quantities, and stored up in the liquid form, in strong wrought-iron vessels. The apparatus used for this pur-

pose was devised by Thilorier. A modification of it is represented in fig. 151. It consists of two very strong hollow cylinders of wrought-iron, one of which, A, is employed as a retort for generating the gas; the other, B, is a receiver, in which it is accumulated. The generator, A, is charged with a mixture of 1·25 kilos. ($2\frac{3}{4}$ lb.), of finely powdered hydric sodic carbonate (the common bicarbonate of soda) ($NaHCO_3$), and 2·83 litres ($6\frac{1}{4}$ lb.) of warm water: a copper tube, C, containing 0·68 kilo. ($1\frac{1}{2}$ lb.) of oil of vitriol, is cautiously introduced, and the head of the apparatus, furnished with a stop-cock of peculiar construction, is screwed down and rendered tight by a leaden washer. The generator is then reversed, so as to mix the materials, which, by their reaction, liberate carbonic anhydride; this gas accumulates in the upper part of the vessel, where it is liquefied by its own pressure; a strong tube, E, is screwed on laterally to both vessels, A and B, in order to connect them together. The receiver, B, is kept cool by being immersed in melting ice. As soon as the stop-cocks are opened, the liquefied gas distils over; the stop-cocks are then closed, the vessels A and B are separated, and a fresh charge is introduced into the generator.* The same operations are then repeated, until a sufficient quantity of the liquefied gas has been obtained. Communicating with the stop-cock of the receiver is the tube, *b*, which passes down nearly to the bottom of the vessel, and terminates in an open end, so that as soon as the stop-cock is opened, a jet of the liquid anhydride is, by the pressure of its own vapour, forced up the vertical tube, *b*, and it escapes from the vessel through a fine nozzle, *e*, which is screwed to the stop-cock. The issuing liquid immediately begins to evaporate with great rapidity; by this means so large a quantity of latent heat is carried off in the escaping gas, that a portion of the liquid is converted into the solid form. If the jet of liquid be made to play into a cylindrical box, D, furnished with lateral apertures for the free passage of the gas, the solidified anhydride may be collected in the form of a flocculent deposit, of snowy whiteness, which gradually evaporates in the air, without undergoing previous liquefaction. This may be seen by placing a few flakes of the solid in a retort, the mouth of which is immersed in water: the gas, as it rises in bubbles, can thus be collected.

FIG. 151.



If means be taken to cut off the supply of heat from external objects by placing the solidified anhydride in a glass vessel,

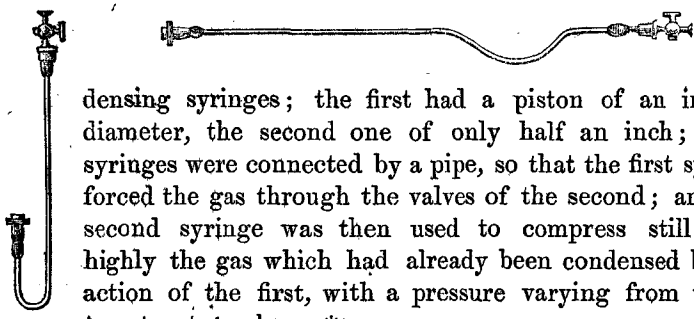
* By attaching a condensing syringe to the bottom of the generator, by means of which water may be pumped into the vessel, Mr. Addams displaced the condensed gas, and thus saved a considerable portion which would otherwise have been lost.

covered externally with flannel, enclosing this in a second glass, and covering the whole with a card, and thus making, in fact, an extemporaneous ice-pail, the solidified anhydride may be kept in open air for some hours. As will readily be supposed, the temperature of this solid is extremely low. According to the experiments of Faraday, it is as much as $-106°$ ($-77°$ C.). It may, notwithstanding, be handled with impunity, and may be put into water, without causing the water to freeze. These paradoxical effects are, however, easily explained. The cold solid never really touches either the water or the hand, because owing to the rapidity with which it evaporates, it is constantly surrounded by a badly conducting atmosphere of its own vapour; but if it be really brought into contact with any solid or liquid, which may be done by moistening the solid anhydride with ether, which has a strong adhesion to carbonic anhydride, its low temperature is at once manifested, and this low temperature is maintained by its continual evaporation, which constantly carries off a large quantity of heat in the latent state. By placing some mercury in a basin, pouring on it a small quantity of ether, and adding a little solidified carbonic anhydride, the mercury will, in a few seconds, be converted into a malleable solid, although before the metal will freeze it is necessary that the temperature be reduced as low as $-37°{\cdot}9$ ($-38{\cdot}8°$ C.). If the frozen mercury be transferred to a vessel containing a small quantity of water, the metal will be quickly thawed, but spiculæ of ice will be formed, showing that the process of liquefaction in the case of mercury, as in all other instances, is attended with a disappearance of heat.

By accelerating the evaporation of the bath of carbonic anhydride and ether, Faraday was enabled to command a still greater reduction of temperature, and in the vacuum of the air-pump he obtained by this means a degree of cold which he estimated at $-166°$ ($-110°$ C.). In such a cold bath, many of the liquefied gases were frozen, and were obtained in the shape of solids, clear and transparent as ice. Among the number which assumed this form was carbonic anhydride itself. (*Phil. Trans.* 1845, 155.) Even without the aid of pressure, but simply by employing a bath of carbonic anhydride and ether in the air, the following gases—viz., chlorine, cyanogen, ammonia, sulphuretted hydrogen, arseniuretted hydrogen, hydriodic acid, hydrobromic acid, and carbonic anhydride—were obtained in the liquid form, and were sealed up in tubes. The tubes used were of green bottle-glass, bent as represented in fig. 152; to these tubes brass caps and stop-cocks were, when necessary, securely attached, by means of a resinous

cement. The cold bath was applied at the curvature. When pressure was requisite, it was obtained by the employment of two con-

FIG. 152.

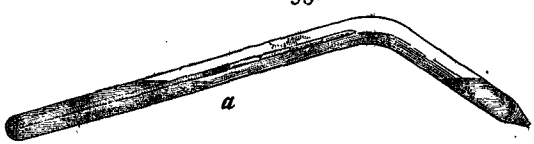


densing syringes; the first had a piston of an inch in diameter, the second one of only half an inch; these syringes were connected by a pipe, so that the first syringe forced the gas through the valves of the second; and the second syringe was then used to compress still more highly the gas which had already been condensed by the action of the first, with a pressure varying from ten to twenty atmospheres.*

Natterer obtained a still more intense degree of cold than that produced by carbonic anhydride and ether *in vacuo*, by mixing liquid nitrous oxide with carbonic disulphide and placing the bath *in vacuo*; the lowest temperature which he has recorded is $-220°$ ($-140°$ C.). Silicic fluoride, at this point, became a transparent solid, but liquid chlorine and carbonic disulphide preserved their fluidity. (*Liebig's Ann.* 1845, liv. 254.)

(197) *Pressure exerted by Condensed Gases.*—In order to estimate the pressure of the condensed gas in the vessel in which it was contained, Faraday made use of small air-gauges, which he enclosed in the tubes employed for the condensation (fig. 153). These gauges consisted of a somewhat conical capillary tube of glass, which was divided into parts of equal volume by introducing into the tube a globule of mercury shown at *a*, and causing it to occupy each part of the tube in succession: the length of the little cylinder into which the mercury was reduced in each portion of the tube was marked upon the glass with black varnish. The mercury was then transferred towards the widest extremity,

FIG. 153.



* The temperatures recorded in these experiments are in all probability somewhat too high. They were estimated by means of a spirit thermometer, divided into degrees below 32° F., 'equal in capacity to those between 32° and 212°;' but the contraction of alcohol is more rapid at low than at high temperatures: at the lowest temperatures attained, the alcohol became somewhat viscid.

and the tube was sealed at its narrow end. A known quantity of air was thus included, and, by the compression which this air experienced in the course of the experiment (the volume being inversely as the pressure), the pressure of the gas under examination was easily calculated. It is remarkable that many of these condensed liquids expand upon the application of heat more rapidly than the gases themselves. It has been also found that Boyle's law (27), that the volume of a gas varies in the inverse ratio of the external pressure, is only approximately true in the ordinary gaseous state. The general law connecting pressure and volume, according to the recent experiments of Andrews on carbonic anhydride, is expressed by the equation $v\ (1 - p\ v) = c$, where v is the volume of the gas, p the external pressure, and c a constant for a given temperature. It follows that for homologous points, at which $p\ v = p'\ v'$, in any two given isothermals, the ratio of the external pressures is constant (*Phil. Trans.* 1876, 444, 447). See also *notes*, pages 50 and 293.*

Although indications of this departure from Boyle's law have been observed at common temperatures with some of the more condensible gases, such as sulphurous anhydride, sulphuretted hydrogen, cyanogen, and ammonia, it was most distinctly exhibited in the experiments of Cagniard de La Tour (*Ann. Chim. Phys.* 1822, xxi. 127, 178, and 1823, xxii. 410). De La Tour partially filled some strong glass tubes with water, with alcohol, with ether, and with some other liquids, furnished them with gauges, and sealed them hermetically. He then cautiously raised the temperature. The alcohol (density 0·844), which occupied $\frac{2}{3}$ the capacity of the tube, gradually expanded to double its volume, and then suddenly disappeared in vapour, at a temperature of 497°·7 (258°·7 C.); it then had a pressure of about 119 atmospheres. Ether became gaseous at 392° (200° C.), in a space less than double its original volume, having a pressure of 37·5 atmospheres; whereas, if Boyle's law held good in these cases, calculating from the volume of vapour which a certain bulk of each liquid yields under the atmospheric pressure, ether should have exerted a pressure equal to about 190 atmospheres, and alcohol of at least 300. Water was found to become gaseous in a space equal to about four times its original volume, at a temperature of about 773° (412° C.), (that of melting zinc). So great was the solvent

* The experiments of Fairburn and Tate on the pressure of superheated steam (*Phil. Trans.* 1860, 190) show that this diminution of elasticity near the point of condensation is very appreciable in the case of aqueous vapour.

power of water on glass, at this high temperature, that the addition of a little sodic carbonate was necessary to diminish the action on the glass, which frequently gave way until this expedient was adopted. As the vapours cooled, a point was observed at which a sort of cloud filled the tube, and, in a few moments after, the liquid suddenly reappeared.

It will be seen from the subjoined Table, that even after the liquid has wholly disappeared, the increase in the pressure of the

Cagniard de La Tour's Experiments.

Temperature.		Ether.		Carbonic disulphide.
		Volume, as liquid 7 parts, as vapour 20 parts.	Volume, as liquid 3½ parts, as vapour 20 parts.	Volume, as liquid 8 parts, as vapour 20 parts.
°C.	°F.	Pressure in atmospheres.	Pressure in atmospheres.	Pressure in atmospheres.
100	212	5·6		4·2
112·5	234·5	7·9		5·5
125·0	257	10·6	14·0	7·9
137·5	279·5	12·9	17·5	10·0
150·0	302	18·0	22·5	13·0
162·5	324·5	22·2	28·5	16·5
175·0	347	28·3	35·0	20·2
187·5	369·5	37·5*	42·0*	24·2
200·0	392	48·5	50·5	28·8
212·5	414·5	59·7	58·0	33·6
225·0	437	68·8	63·5	40·2
237·5	459·5	78·0	66·0	47·5
250·0	482	86·3	70·5	57·2
262·5	504·5	92·3	74	66·5*
275·0	527	104·1	78	77·8
287·5	549·5	112·7	81	89·2
300·0	572	119·4	85	98·9
312·5	594·5	123·7	89	114·3
325·0	617	130·9	94	129·6
331·2	628·2			135·5

vapour, as the temperature rises, is as rapid as before it had all volatilized, and indeed it continues to increase at a rate far greater than that which would be produced in air by an equal elevation of temperature. Atmospheric air, under a pressure of 37·5 atmospheres at 370° (188° C.) would at 482° (250° C.), have a pressure of 42·5, and at 617° (325° C.) of 48·6 atmospheres, whereas the corresponding pressures with ether were 86·3 and 130·9 atmospheres. In the case of the two experiments with ether, the increase in pressure is greatest at first in the tube which contains

* At this point the liquid had entirely disappeared as vapour.

the smallest proportion of liquid; probably because the influence of cohesive attraction is more completely overcome in the tube which admits of the greatest distance between the particles of the vapour, though at higher temperatures the pressure increases less rapidly in this tube than in the other.

Space must always be allowed for the full expansion of the liquid, otherwise the strongest vessels will give way.

Andrews has observed, that on partially liquefying carbonic anhydride by pressure alone, in his apparatus, and gradually raising at the same time the temperature to 88° (31° C.), the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 31° C., no apparent liquefaction of carbonic anhydride or separation into two distinct forms of matter could be effected, even when a pressure of 300 or 400 atmospheres was applied, and, in consequence, Andrews calls temperature of 31° (or more accurately 30°·92) the critical point for carbonic anhydride. If a quantity of carbonic anhydride at the temperature of 31°·1 be submitted to pressure, its volume diminishes regularly until the pressure reaches 73 atmospheres; a slight increase of pressure now causes a rapid diminution of volume, but without any appearance of liquefaction. If the experiment be repeated at higher temperatures, the pressure at which this sudden contraction takes place will be found to be higher and higher until at 48°·1 the sudden contraction has disappeared, and the volume diminishes regularly as in the case of a permanent gas, though at a more rapid rate. Nitrous oxide gave analogous results.*

From the foregoing experiments, it is obvious that there exists for every liquid a temperature at which no amount of pressure is sufficient to retain it in the liquid form. It is not surprising, therefore, that mere pressure, however great, should fail to liquefy many of the bodies which usually exist in the form of gases.

The following Table embodies the results obtained by Faraday on the condensation and solidification of the gases. The solids were usually denser than the liquid portions from which they separated.

* Information by letter from Dr. Andrews, since published as the Bakerian Lecture of 1869. (*Proc. Roy. Soc.* 1869, xviii. 42, and *Phil. Trans.* 1869, 575.)

Condensation and Solidification of Gases.

Names of the Gases.	Melting Point.		Pressure in Atmospheres.			
	° C.	° F.	at −17·8° C. at 0° F.	at 0° C. at 32° F.	at 15°·5 C. at 60° F.	° F.
Sulphurous Anhydride	− 76·1	− 105	0·72	1·53	2·54	5·16 at 100°
Cyanogen	− 34·4	− 30	1·25	2·37		4·00 at 63°
Hydriodic Acid	− 51·1	− 60	2·9	3·97	5·86	
Ammonia	− 75	− 103	2·48	4·44	6·90	10·00 at 83°
Sulphuretted Hydrogen	− 85·5	− 122	6·0	10·0		14·60 at 52°
Nitrous Oxide	− 101·1	− 150	19·0	32·0		33·40 at 35°
Carbonic Anhydride ...	− 56·7	− 70	22·8	38·5		
Euchlorine	− 59·4	− 75				
Hydrobromic Acid ...	− 86·7	− 124				
Silicic Fluoride	− 140	− 220				
Chlorine						
Arseniuretted Hydrogen			5·21	8·95	13·19	
Phosphuretted Hydrogen						
Olefiant Gas			27·2			
Boric Fluoride						11·54 at − 62°
Hydrochloric Acid ...			15·0	26·20		40·00 at 50°

The diagram on the opposite page (fig. 154) shows the curves indicating the increase of pressure with the temperature, from Faraday's tables. In this diagram, the vertical lines represent the degrees of temperature on Fahrenheit's scale; the horizontal lines show the pressure in atmospheres exerted by the condensed gas. The numbers attached to each curve correspond to the gases in the following order :—

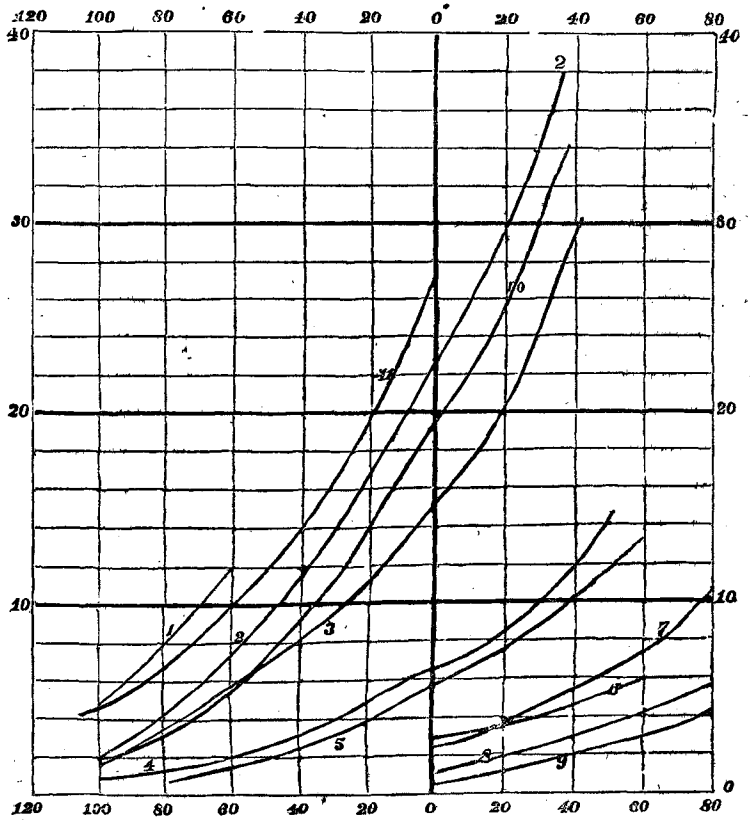
1. Boric Fluoride.
2. Carbonic Anhydride.
3. Hydrochloric Acid.
4. Sulphuretted Hydrogen.
5. Arseniuretted Hydrogen.
6. Hydriodic Acid.
7. Ammonia.
8. Cyanogen.
9. Sulphurous Anhydride.
10. Nitrous Oxide.
11. Olefiant Gas.

Faraday remarks, that as far as his observations go, 'it would appear that the more volatile a body is, the more rapidly does the force of its vapour increase by further addition of heat, commencing at a given point of pressure; for all these, for an increase of pressure from two to six atmospheres, the following number of degrees require to be added for the different bodies named :— Water, 69° F.; sulphurous acid, 63°; cyanogen, 64°·5; ammonia, 60°; arseniuretted hydrogen, 54°; sulphuretted hydrogen, 56°·5; muriatic acid, 43°; carbonic acid, 32°·5; nitrous oxide, 30°.' (*Phil. Trans.* 1845, 176.)

The pressures indicated by the curves in fig. 154, after all, are probably only approximations. The experiments of Cagniard de La Tour show that under these enormous pressures the volume which the liquid bears to the space in which it is confined has a

material influence upon the pressure which its vapour exerts when the results of different experiments with the same liquid are compared at the same temperatures, and before the liquid has wholly assumed the state of vapour; this will be seen by comparing the two columns showing the pressure of ether at temperatures below 187° C. in two different experiments (page 414). It is very probable that the extraordinary discrepancies in the

FIG. 154.



estimates of the pressure of liquefied carbonic anhydride given by Faraday, Thilorier, and Addams, are due to this cause. Similar differences, to a less extent, have been observed in the case of sulphurous anhydride, and cyanogen, and some other gases.

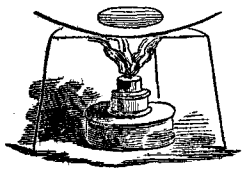
Faraday states, as the results of his experiments, that ammonia and sulphuretted hydrogen, when solidified, each furnished a white translucent mass, like fused ammonic nitrate: euchlo-

rine gave a transparent orange-coloured crystalline solid. The other liquefied gases which were susceptible of solidification furnished colourless transparent crystalline masses like ice. The specimens of phosphuretted hydrogen, nitrous oxide, and olefiant gas, upon which he operated, although prepared with care, consisted of a mixture of two gases, one considerably more condensible than the other.

Six gases—viz., oxygen, hydrogen, nitrogen, nitric oxide, carbonic oxide, and marsh gas—have resisted all attempts to liquefy them. Faraday found that oxygen remained gaseous under a pressure of 27 atmospheres, at a temperature of $-166°$ ($-110°$ C.); and a pressure of 58·5 atmospheres at $-140°$ ($-96°$ C.) was equally ineffectual in producing its liquefaction. Nitrogen and nitric oxide resisted a pressure of 50 atmospheres: with carbonic oxide, a pressure equivalent to that of 40 atmospheres; with coal gas, one of 32; and with hydrogen, one of 27 atmospheres, was applied without effecting the liquefaction: in all these experiments the temperature was maintained at $-166°$ ($-110°$ C.). Andrews (*Report Brit. Assoc.* 1861, 2nd part, 76) has succeeded in applying to these gases still greater pressures than any recorded by Faraday, without producing liquefaction, although a bath of ether and carbonic anhydride was employed: air was reduced to $\frac{1}{67.5}$ of its original volume, oxygen to $\frac{1}{55.4}$, hydrogen to $\frac{1}{50.6}$, carbonic oxide to $\frac{1}{27.8}$, and nitric oxide to $\frac{1}{68.0}$ of its original volume. Hydrogen and carbonic oxide departed less from Boyle's law than oxygen and nitric oxide.

(198) *Spheroidal State produced by Heat.*—Much attention has of late years been excited by a phenomenon first described in 1756 by Leidenfrost, and which has been made the subject of careful investigation by Boutigny (*Ann. Chim. Phys.* 1843 [3], 350, and 1844 [3], 16). The following experiments will illustrate its character. If a good conductor, such as a sheet of metal, be heated to between 150° and 200° C., and water be allowed to fall upon its surface, the liquid does not enter into ebullition; but instead of wetting the surface as usual, it rolls about in spheroidal masses in the manner shown in fig. 155; the temperature of such a spheroid never rises to the boiling-point of the liquid.* If the source of heat be

FIG. 155.



* Colley (*Pogg. Ann.* 1871, cxliii. 125–141) has found that in the case of water, the temperature of the spheroid may vary between 90°·56 and 100°·34,

removed, the temperature will fall, until a point is at length reached when the liquid suddenly begins to boil vehemently, and is dispersed in all directions with a loud hissing noise.

This phenomenon is a complicated result of at least four distinct causes. Of these the most influential is the repulsive force which heat exerts between objects which are closely approximated to each other. A low manifestation of this action has been already noticed when speaking of the effect of a rise of temperature in producing a decrease of capillary attraction (51). When the temperature reaches a certain point, actual repulsion between the particles ensues. Besides this repulsion occasioned by heat, the other causes which may be mentioned as tending to produce the assumption of the spheroidal condition by the liquid, are these:—1. The temperature of the plate is so high that it immediately converts any liquid that touches it into vapour, upon which the spheroid rests as on a cushion. 2. This vapour is a bad conductor of heat, and prevents the rapid conduction of heat from the metal to the globule. 3. The evaporation from the entire surface of the liquid carries off the heat as it arrives, and assists in keeping the temperature below the point of ebullition. The drop assumes the spheroidal form as a necessary consequence of the cohesion among the particles of the liquid, and the simultaneous action of gravity on the mass.

Boutigny finds that even if the liquid be boiling, its temperature sinks from 3° to 4° C. below its boiling-point at the moment that it falls on the heated surface, and takes the spheroidal form.

All liquids are capable of assuming this condition; but the temperature to which it is necessary to heat the conducting surface varies with each liquid; the lower the boiling-point of the liquid, the lower also is the required temperature. The exact degree is dependent partly upon the conducting power of the plate, and partly upon the latent heat of the vapour; the temperature of the plate approaches the boiling-point of the liquid more closely as the latent heat is less.

Boutigny considered the temperature of each liquid, when in the spheroidal state, to be as definite as that of its boiling-point. Boutan has, however, shown that these temperatures are liable to slight variations. The following table shows the lowest tempera-

---

according to the size of the drop and the temperature of the vessel containing it; the larger the spheroid, the higher the temperature. The distance between the heated vessel and the spheroid when the latter weighed from 1 to 1·5 grm., was estimated at 0·15 to 0·25$^{mm.}$.

ture of the plate and the temperature of the spheroid for certain liquids, according to Boutigny :—

Liquid employed.	Temperature of Plate.		Temperature of Spheroid.	
	° F.	° C.	° F.	° C.
Water	339·8	171	205·7	96·5
Alcohol	273·2	134	167·9	75·5
Ether	141·8	61	93·6	34·2
Sulphurous anhydride			13·1	− 10·5

Even *in vacuo* the spheroidal state is observed to occur when the liquid is allowed to fall upon a plate sufficiently heated. Solids in liquefying in hot capsules, pass into this same state, as is well exemplified by throwing a few crystals of iodine upon the heated surface. Provided that the hot surface be a sufficiently good conductor of heat, the nature of the material is unimportant. Silver, platinum, copper, and iron may all be successfully used. Tomlinson has shown that even one liquid may be thrown into the spheroidal form on the surface of another, as water, alcohol, or ether, on the surface of hot oil; but this experiment requires care, otherwise the water sinks in the oil, evaporation from the surface of the drop is prevented, steam is generated with explosion, and the hot oil is scattered about in all directions.

If the hot metal be sufficiently massive, a large body of water may be converted into the spheroidal state. Boutigny has suggested that in certain cases the explosion of steam-boilers may have been due to this cause. It is indeed quite possible, although such an occurrence must be rare, that the water may be all expended in a boiler beneath which a brisk fire is maintained, so that the mass of metal may become intensely heated. On the admission of cold water under such circumstances, it would at first assume the spheroidal state, and as the boiler gradually cooled down, by the introduction of more water, a sudden and uncontrollable burst of vapour would ensue. The safety-valve in such a case would be inadequate to allow the needful escape for the immense quantity of steam which would be instantaneously generated, and an explosion would probably occur.

By tracing the effects above detailed to their extreme consequences, some singular and paradoxical effects have been produced. For example, liquid sulphurous anhydride becomes spheroidal in a red-hot capsule at a temperature of about 14° (− 10° C.), or considerably below the freezing-point of water. If a little water be dropped into this spheroid, the temperature of the water is instantly reduced below its freezing-point, and a mass of ice is

formed within the glowing crucible. If a bath of solid carbonic anhydride and ether be substituted for the sulphurous anhydride in the red-hot capsule, mercury placed within it in the bowl of a small spoon may be frozen with equal certainty. But perhaps the most marvellous result is the impunity with which the moistened hand may be plunged for an instant into molten lead, or even into cast iron as it issues from the furnace. In these cases the adhering moisture is converted into vapour, which forms an envelope to the skin sufficiently non-conducting to prevent the passage of any injurious quantity of heat during the brief immersion. An ingenious application of this principle has long been employed in the glass-house. In first rudely shaping the large masses of glass which are to be blown into shades, and into cylinders which are afterwards flattened into the heavy sheets technically termed British plate, open hemispherical wooden moulds are used to give the globular form; in order to prevent the wood from being burned, the workman pours a little water into the mould; it protects the wood, but assumes the spheroidal form, and neither touches nor injuriously cools the molten glass.

§ IV. Atomic relations of heat of combination.

(199) *The quantity of Heat developed by Chemical Action is definite.*—The last subject to which we shall here advert in connexion with heat, is to the chemist perhaps the most directly interesting of any, on account of its direct quantitative relations to chemical action. Experiment has proved that the amount of heat which each element emits when entering into combination is definite, and has a specific relation to the combining number of each substance. When the same substance is burned with a due supply of oxygen, and with suitable precautions, a given quantity of it always emits the same amount of heat. Thus 1 gramme of hydrogen, when burned in oxygen, always emits heat enough to melt 434·85 grammes of ice; 31 grammes of phosphorus, when burnt to phosphoric anhydride, yields heat sufficient to melt 2248 grammes of ice; and 12 grammes of carbon, when converted into carbonic anhydride, emits heat sufficient to melt 1223·5 grammes of ice. It would at first sight appear easy to determine by direct experiment the amount of heat which each body emits in the act of combining with an atom of oxygen, and to compare the results thus obtained with a corresponding series of experiments made by combining the same elements with an equivalent proportion of chlorine, of bromine, or of other elements.

In reality, however, it is not so; for, independently of the difficulties which the exact admeasurement of heat always involves, there are others which will be rendered evident by considerations such as the following.

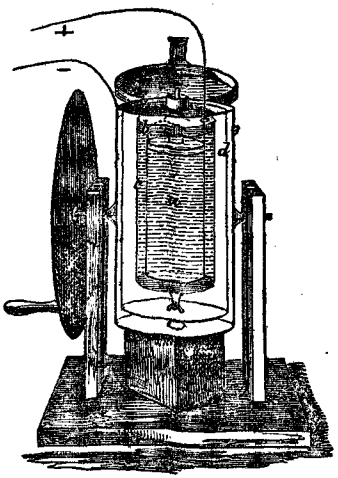
Scarcely any molecular change can take place without either evolution or absorption of heat. When a gas or a vapour becomes liquefied or solidified, the change of state is always attended by the evolution of the heat which it previously contained in a latent state (177), and the effect is reversed when a solid passes into the liquid or the aëriform condition, heat being then absorbed (174, 178). Now, the instances in which chemical combination takes place without any alteration in the physical condition of bodies are rare, and the cases in which the product occupies exactly the same volume as the bodies from which it was formed, are still more so. When two gaseous elements, like chlorine and hydrogen, unite and form a compound which is not only gaseous but which occupies the same volume as the bodies did before their combination, the problem is presented in the simplest form: the heat observed in such a case is due solely to the chemical action; but when the products, though gaseous, occupy a smaller volume after they have entered into combination,—as when 2 volumes of carbonic oxide unite with 1 volume of oxygen, and form but 2 volumes of carbonic anhydride,—the heat emitted during the act of combination is due partly to chemical action, and partly also to the condensation which the gases have experienced. When the product assumes the liquid state, as occurs in the formation of water during the combustion of hydrogen in oxygen, the quantity of heat emitted owing to this change of state is still more considerable. When, on the other hand, the solid passes into the aëriform state, as when carbon is converted into carbonic anhydride, the heat actually observed is less than that which the combination ought really to produce: and the effect is reversed when the solid state is assumed by the product, as when phosphorus becomes oxidized to phosphoric anhydride; in which case the heat evolved exceeds that really due to the act of combination. But even when no change of state is observed, minor disturbing causes are at work. Supposing it were possible to obtain a direct combination of iodine with a metal, such as iron or zinc; even then, though two solids united to form a third solid, it would not necessarily happen that the whole of the heat emitted was due to the chemical action. If zincic iodide, for example, contracted in the act of combination, a small portion of the heat observed would be due to that evolved by the solid in consequence

of its change of volume; whereas, if the iodide occupied a larger space after combination than that of the two elements separately, the heat observed would be less than that resulting from the chemical action: and even if no change of volume occurred, it might happen that the compound had a specific heat different from that of the original elements, and in such case a slight elevation or depression of temperature might be occasioned, which was not really the chemical result of the act of combination.

From the foregoing statement it is therefore clear that the experimental numbers, however carefully the observations are made, can very rarely yield the actual quantities of heat due to chemical actions: they are compound results from which the true *calorific equivalents* of the different elements (or heat evolved by the combination of chemical equivalents of the different elements) must be deduced by other means.

(200) *Early Experiments.*—The importance of determining accurately the amount of heat arising from chemical action was first distinctly announced by Lavoisier, who instituted a series of experiments with the view of finding the quantity of heat evolved during the combustion of various substances: his method consisted in ascertaining the quantity of ice that was melted, when known quantities of these bodies were burned in his calorimeter. The first experiments with any claim to accuracy, however, are those of Dulong, which have formed the foundation for all subsequent researches upon the subject. Important additional investigations have since been made, particularly by Despretz, and more recently by Andrews, by Favre and Silbermann, by Berthelot, and by Thomsen.

FIG. 156.



(201) *Researches of Andrews.*—The apparatus employed by Andrews in these experiments (*Phil. Mag.* 1848 [3], xxxii. 321, 426) was of a simple kind. When the substances to be combined were in the gaseous state, and the products of combustion were also gaseous, the two gases were mixed in the proper proportions, as in the performance of eudiometric experiments, and introduced into a vessel of thin sheet copper (*a*, fig. 156), of a capacity of about 23 cubic inches (380 cubic centim.). It was closed by a

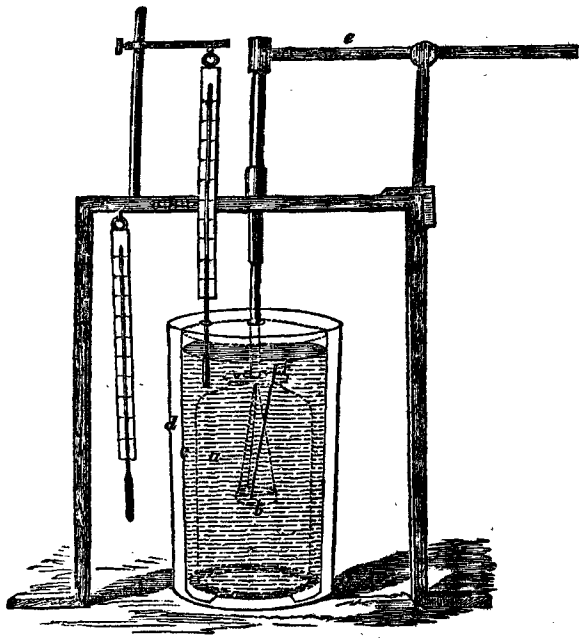
screw, the head of which was perforated to admit a cork, through which a silver wire, *b*, passed; this wire was connected by a thin platinum wire within the vessel to a second silver wire soldered to the screw itself. The platinum wire could be ignited by connecting it for an instant with a small voltaic battery, and thus the gaseous mixture could be detonated at the pleasure of the operator. The copper vessel containing the mixed gases was then introduced into a larger vessel, *c*, which was filled up with a known quantity of water: the vessel, *c*, was suspended in a cylinder, *d*, provided with a moveable cover, and the whole was enclosed in an outward cylindrical vessel, *c*, arranged so as to admit of its being made to rotate upon its shorter axis.

The apparatus having been mounted, was caused to rotate, in order to bring every part to a uniform temperature: after which the exact amount of this initial temperature was read off by a very sensitive thermometer, capable of indicating differences of temperature of $\frac{1}{500}$ of a degree Centigrade. The thermometer was then withdrawn, and the gases exploded by igniting the fine platinum wire; the outer vessel of water was closed by a cork, and the apparatus was caused to rotate for thirty-five seconds, in order to establish an equilibrium of temperature in all its parts. The thermometer was again introduced, and the rise of temperature was ascertained. After this observation the apparatus was again made to rotate for thirty-five seconds, and the loss of heat thus occasioned was ascertained. This third rotation was necessary in order to determine the cooling effect of the atmosphere upon the apparatus, during the time that the experiment lasted; in these cases it seldom amounted to more than $\frac{1}{400}$ of the total quantity of heat set free.

When solid bodies were burned in oxygen, the form of the apparatus was modified; the combustion was effected in a copper vessel (*a*, fig. 157), of about 4 litres, or 250 cubic inches in capacity, which was filled with oxygen: and a known quantity of the combustible was supported in a small platinum dish, *b*; when all was ready, the vessel *a* having been accurately closed, the combustible was ignited by means of a voltaic current sent through a very fine platinum wire in connexion with the insulated wire *f*. Previously to this ignition, the vessel *a* was immersed in a large cylinder *c*, filled with a known quantity of water, and the whole was surrounded by an outer vessel of tin-plate *d*, to prevent radiation. The copper vessel could be agitated within the vessel of water by means of the lever *e*. Particular expedients were required in certain cases to ensure the ignition: for instance, in

burning zinc filings and other metals in oxygen, a minute portion of phosphorus was employed to kindle the metal; the weight of this piece of phosphorus being known, the heat which it emitted

FIG. 157.



was calculated, and deducted from that observed. In some cases these experiments lasted fifteen or sixteen minutes, so that the correction for the cooling effect of the external air acquired considerable importance.

When chlorine was used instead of oxygen, it was not necessary to ignite the substance under trial: but in order to prevent the spontaneous ignition of the body, the latter was enclosed in a thin glass bulb, which was broken by agitation of the apparatus at the moment that everything was prepared. The chlorine itself was in most instances contained in a glass vessel, which was filled with the gas by displacement; an excess of the body for combination with the chlorine was always employed, so as to ensure the total absorption of the chlorine. The time allowed for absorption was in each case six minutes and a half.

(202) *Experiments of Favre and Silbermann.*—A very extensive series of researches upon the development of heat during molecular and chemical changes were undertaken by Favre and Silber-

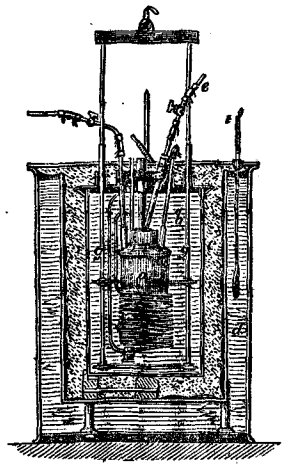
Heat developed during Combustion in Oxygen.

Substance burned.	Heat units. Grammes of water raised 1° C., by 1 gramme of each substance.	Grammes of water raised 1° C., by combination of 1 gramme of oxygen.	Calorific equivalent. Grammes of water raised 1° C., for 8 grammes (1 eqt.) of oxygen.	Compound formed.	Observer.
Hydrogen	*34462	4308	34462	H_2O	Favre & Silbermann.
„	*33808	4226	33808	„	Andrews.
„	*34672	4334	34672	„	Dulong.
Carbon	*8080	3030	24240	CO_2	Favre & Silbermann.
„	*7900	2962	23700	„	Andrews.
„	*7914	2968	23742	„	Despretz.
Sulphur	*2220	2220	17760	SO_2	Favre & Silbermann.
„	*2307	2307	18456	„	Andrews.
„	*2601	2601	20808	„	Dulong.
Phosphorus	*5747	4454	35631	P_2O_5	Andrews.
„	*5669	4394	35148	„	Abria.
Zinc	1305	*5301	42408	ZnO	Andrews.
„	1304	*5299	42393	„	Dulong.
Iron	1575	*4134	33072	Fe_3O_4	Andrews.
„	1656	*4348	34782	„	Dulong.
Cobalt	1085	*4001	32010	? CoO	„
Nickel	1011	*3730	29839	NiO	„
Tin	1234	*4552	36417	SnO_2	„
„	1147	*4230	33840	„	Andrews.
Antimony	984	*3753	30023	Sb_2O_4	Dulong.
Copper	604	*2394	19152	CuO	Andrews.
„	623	*2470	19758	„	Dulong.
Carbonic oxide ...	*2495	4367	34937	CO_2	„
„ ...	*2431	4254	34034	„	Andrews.
„ ...	*2403	4205	33642	„	Favre & Silbermann.
Stannous oxide ...	535	*4480	35841	SnO_2	Dulong.
„ ...	519	*4349	34792	„	Andrews.
Cuprous oxide ...	256	*2288	18304	CuO	„
„ ...	245	*2189	17513	„	Dulong.
Cyanogen	*5267	4280	34236		„
Marsh gas	*13063	3266	26126		Favre & Silbermann.
„ ...	*13376	3344	26751		Dulong.
„ ...	*13108	3277	26216		Andrews.
Olefiant gas ...	*11942	3483	27865		„
„ ...	*11858	3459	27669		Favre & Silbermann.
„ ...	*12227	3566	28531		Dulong.
Alcohol	*6909	3311	26485		„
„	*6850	3282	26258		Andrews.
„	*7183	3442	27535		Favre & Silbermann.
Ether	*9027	3479	27834		„ „
Olive oil	*9862				Dulong.
Oil of turpentin ...	*10852	3294	26355		Favre & Silbermann.
Carbonic disulphide	*3401	2692	21540		„ „

* Experimental numbers: the figures on the same line are obtained by calculation.

mann (*Ann. Chim. Phys.* 1852 [3], xxxiv. 357 ; xxxvi. 5, and 1853 ; xxxvii. 406). These experiments were conducted in many cases upon a larger scale than those of Andrews, and with a much more elaborate apparatus. It is satisfactory to find, however, that their experimental results generally agree pretty closely with those of Andrews, although they differ from him in some of their deductions. The essential part of Favre and Silbermann's apparatus was a vessel of brass gilt, *a*, fig. 158, in which the combustions were performed; this vessel was immersed in a calorimeter, *b*, of silvered copper, which contained about 2 litres of water. The calorimeter was supported in an outer vessel, *c*, lined with swan's down, and this case was itself surrounded by an outer double envelope, *d*, filled with water. It was found that by these means the loss of heat from the influence of the external atmosphere was reduced to a very small and measurable amount. When the combustions were performed in oxygen, this gas, previously dried, was allowed to flow into the combustion-chamber by the tube *e*, and the gases produced, together with the superfluous oxygen, were forced, before their exit from the apparatus, to traverse a spiral tube of thin copper, *f*, so that they might be completely cooled down to the temperature of the water in the calorimeter, *b*; *g g* is an agitator for ensuring uniformity of temperature in the water of the calorimeter.

FIG. 158.



Solid bodies were kindled by the introduction of small pieces of burning charcoal; liquids were burnt in small lamps with asbestos wicks, and gases were introduced by a jet previously set on fire. The apparatus in the figure shows the arrangement for burning carbon; the scale of the thermometers employed allowed a variation of $\frac{1}{160}$ of 1° C. to be estimated. In most cases the weight of the substance burned was ascertained by collecting and weighing the products of combustion.

(203) *Quantities of Heat evolved during Combustion.*—The preceding Table is compiled chiefly from the results of Dulong, Andrews, and Favre and Silbermann. It is founded upon the direct results obtained by the rapid combustion, in oxygen, of the various substances enumerated in the first column. The *heat unit* adopted is the one proposed by Dulong, viz., the quantity of heat

required to raise 1 gramme of water 1° C., or rather from 0° C. to 1° C. The second column indicates the units of heat evolved during the act of combustion; or the number of grammes of water which would be raised from 0° C. to 1° by the combustion of 1 gramme of each substance. The third column indicates the number of grammes of water heated to the same amount by the combination of 1 gramme of oxygen with each body; and the fourth column (the *calorific equivalent*) is obtained by multiplying the numbers in the third column by 8 (the *equivalent* number of oxygen).

Quantities of Heat disengaged by the Action of Chlorine.

Elements operated on.	Grammes of water raised 1° C., by combination of 1 gramme of substance.	Grammes of water raised 1° C., by combination of 1 gramme of chlorine.	Grammes of water raised 1° by combination of 1 eqt. (35·5 grammes) of chlorine.	Compound produced.	Observer.
Hydrogen ...	24006	676	24006	HCl	Abria.
Hydrogen ...	23783	670	23783	„	Favre & Silbermann.
Phosphorus ...	3476 ?	*607	21548	PCl_5 ?	Andrews.
Potassium ...	2679	*2943	104476	KCl	„
Zinc	1559	*1427	50659	$ZnCl_2$	„
Iron	1751	*921	32696	Fe_2Cl_6	„
Tin	1079	*897	31843	$SnCl_4$	„
Antimony ...	751	*860	30530	$SbCl_3$	„
Arsenic ...	1000	*704	24992	$AsCl_3$	„
Copper	962	*859	30495	$CuCl_2$	„
Mercury ...	?	*822	29181	?	„

Quantities of Heat disengaged by the Action of Bromine and Iodine.

Elements operated on.	Grammes of water raised 1° C., by combination of 1 gramme of substance.	Grammes of water raised 1° C., by combination of 1 gramme of bromine or iodine.	Grammes of water raised 1° by combination of 1 eqt. of bromine or iodine.	Compound produced.	Observer.
			Bromine.		
Zinc	1268	*515	41200	$ZnBr_2$	Andrews.
Iron	1277	*298	23840	Fe_2Br_6	„
			Iodine.		
Zinc	821	*210	26670	ZnI_2	„
Iron	463	*68	8636	Fe_2I_6	„

* Experimental numbers.

† *Transactions of the Royal Irish Academy*, 1843, xix. 393.

In some cases the quantity of the combustible was weighed or measured, and in others the quantity of oxygen absorbed was

determined: in the first class of experiments the direct result is contained in the second column, the numbers in the other columns being calculated; and in the second class the experimental numbers are found in the third column. The numbers marked with an asterisk are experimental ones.

The preceding Tables contain the results of a similar series of experiments, in which chlorine, bromine, and iodine were employed instead of oxygen.

From an inspection of these Tables it may be gathered that the quantity of heat disengaged by the following bodies, in their ordinary physical state, during their combination with an equal quantity of oxygen, is nearly the same: viz., hydrogen, carbonic oxide, cyanogen, iron, and tin, to which also may be added stannous oxide and phosphorus, though the heat disengaged by the body last named is somewhat higher than that furnished by any one of the others. If, however, to these numbers the corrections due to the change in the physical state of the products could be applied, the same coincidence would not be observed; but although the trustworthy numerical data required for making these corrections do not exist, it is quite obvious that when equivalent quantities of the different elements unite with equal quantities of oxygen without undergoing change in their physical state, they emit specific, but different amounts of heat. Sulphur, copper, and cuprous oxide disengage little more than half the heat of the substances just mentioned, and carbon is intermediate between these two groups. Zinc gives out more heat than either, and potassium more than zinc.

(204) *Influence of Dimorphism.*—According to the experiments of Favre and Silbermann, equal quantities of the same substance, when in different allotropic conditions, evolve somewhat different amounts of heat during combustion; the modification which is least dense and has the highest specific heat evolving the largest quantity of heat when burned. The following results with carbon, sulphur, and phosphorus, in different states, may be given in illustration of this point:—

	Units of Heat.	Specific Heat.
Diamond evolves	7770	0·14687
Graphite...	7796·6	0·20187
Wood Charcoal	8080	0·24150
Octohedral Sulphur	2220	0·20259
Prismatic	2264	0·1844
Viscous Sulphur	2258	
Red Phosphorus	5070	0·1700
Vitreous Phosphorus	5953	0·1887

Similar differences were observed when different forms of the same compound body were submitted to experiment. According to these observers, heat was evolved during the conversion of aragonite into calc-spar: this is somewhat remarkable, for the density of calc-spar is less than that of aragonite, and hence, from analogy, an absorption of heat was rather to be looked for in this change.

(205) *Heat evolved in certain Cases during Decomposition.*—In the experiments of Dulong it appeared that when carbonic oxide, or hydrogen, was burned in nitrous oxide, a larger amount of heat was evolved than when the same quantities of these gases were burned in oxygen: following up this observation, Favre and Silbermann were led to the remarkable conclusion, that nitrous oxide, in the act of decomposition, evolves a considerable amount of heat; and they estimate that not less than 1154 units of heat are evolved in the separation into its elements of a quantity of nitrous oxide which contains 1 gramme of oxygen. In the decomposition of hydric peroxide also, heat is evolved instead of being absorbed, and they estimate the heat evolved during the liberation of 1 gramme of oxygen from hydric peroxide at 1363 heat units.

Chemists are also familiar with other cases in which decomposition is attended with disengagement of heat; as when the oxides of chlorine, and the so-called iodide and chloride of nitrogen are decomposed. In these cases evolution of light and heat occurs, although the products of decomposition occupy a larger volume than the compound which furnishes them. A still more striking evolution of heat attends the explosive decomposition of gun-cotton, although the gases produced occupy many hundred times the volume of the original substance. The latter case is particularly instructive, for it is obvious that the oxygen and carbon, although present in the compound, are each there in a form in which they retain a large share of heat, ready to be evolved when more intimate chemical union occurs; and it is by no means improbable that these apparent anomalies may be due to the apparent decompositions being truly double decompositions, two new bodies being in each case formed. For example, in the instance of hydric peroxide, the decomposition may be thus represented, $H_2O,O + H_2O,O = 2H_2O + O_2$; where the heat evolved by the union of the two atoms of oxygen may be greater than that absorbed in the decomposition of the hydric peroxide.

(206) *Combustion of Compounds.*—Generally speaking, the

heat given out during the combustion of a compound body is less than that emitted by the combustion separately of a quantity of each of its constituents equal in amount to that present in the compound burnt; but this is not uniformly so, as, for instance, in the case of oil of turpentin, and of carbonic disulphide. Favre and Silbermann have examined the amount of heat developed during the combustion of many hydrocarbons and compound ethers. From these experiments it appears that polymeric bodies* do not emit equal amounts of heat during combustion; but that the denser the vapour which they furnish, the smaller is the amount of heat which they evolve in combining with equal quantities of oxygen. The following Table, which indicates the amount of heat given out by hydrocarbons polymeric with olefiant gas, distinctly shows this:—

		Heat Units.
Olefiant Gas	C_2H_4	11858
Amylene	C_5H_{10}	11491
Paramylene	$C_{10}H_{20}$	11303
Cetene	$C_{16}H_{32}$	11055
Metamylene	$C_{20}H_{40}$	10928

In homologous† compounds, such as the alcohols and the fatty acids, it was also found that for equal quantities of oxygen consumed, the heat of combustion was diminished the oftener that the group of elements (CH_2) entered into the formation of the compound.

Even in metameric bodies—which contain the same number of atoms of the same elements in their molecules, but the atoms arranged in a different order in each compound, and which yield vapours of the same density—the quantity of heat evolved during combustion is not necessarily the same: from which it would appear that differences in the molecular arrangement of the component elements, although the number of the atoms may remain unaltered, may yet produce differences in the amount of heat evolved during oxidation. For example, the following metamerides (all containing $C_3H_6O_2$) evolve different quantities of heat:

		Heat Units.
Propionic acid	$H,C_3H_5O_2$	4670
Formic ether	C_2H_5,CHO_2	5279
Methyl acetate	$CH_3,C_2H_3O_2$	5344

* Bodies which contain centesimally the same proportion of the same elements but which each contain a different number of atoms in their molecule.

† Bodies which have a similar constitution, but which differ in composition by a multiple of CH_2.

(207) *Indirect Methods of Estimating Calorific Equivalents.*—The difficulties experienced in effecting the direct combustion of the metals in oxygen, chlorine, iodine, and sulphur, in such a manner as to ensure the perfect conversion of the metal into a given compound, unmixed with any other body of higher or lower degrees of oxidation, &c., are so considerable, that Favre and Silbermann were led to attempt the solution of this problem by indirect means, upon a principle previously suggested and applied by Dr. Woods (*Phil. Mag.* 1851 [4], ii. 268). An examination of one of the methods employed in the case of the oxides will furnish an idea of the general principle upon which they proceeded.

Whenever a metal is acted upon by an acid, or when one metal is employed to precipitate another metal from any of its salts, as when zinc is dissolved in sulphuric acid, or when copper is precipitated by means of zinc from a solution of its sulphate, heat is evolved. The calorific effects thus obtained are, however, complicated results: for several chemical processes concur in each operation, some of these processes being attended with the absorption, others with the evolution of heat. The calorimeter, of course, only measures the difference of these quantities.

Now, if it be assumed that the quantity of heat which is absorbed when a compound is separated into its elements is the same as that evolved in the formation of that compound, it becomes possible to calculate the value of the calorific action of any one particular chemical operation in the entire process, provided that the heat produced or absorbed in the other portions of the process be determined by other experiments. Suppose, for instance, we take the case of the solution of zinc in dilute sulphuric acid—the elevation of temperature observed will be the resultant of the following operations:—

In the first place, heat is evolved by the combination of an equivalent of zinc with one of oxygen: let this amount of heat $=x$.

Secondly, heat is produced by the solution of the zincic oxide in sulphuric acid: let this $=a$.

Thirdly, heat is absorbed by the separation of the oxygen and hydrogen during the decomposition of a quantity of water equivalent to that of the zinc dissolved: let this $=b$.

If T be the number of heat units indicated by the rise of temperature observed in the calorimeter, supposing a and b to be known from previous experiments, it is obvious that $x = T-a+b$.

Experiment shows that T, the heat evolved during the solution of 1 gramme of zinc, is equal to 567·9 heat units. The solution in sulphuric acid of 1 gramme of zinc after its conversion into oxide, gave for a a quantity equal to 335·54; and b, the heat absorbed during the decomposition of a quantity of water equivalent to a gramme of zinc, was found by another experiment to be equal to 1060·37 units, or

$$\frac{34462}{32{\cdot}5} \text{ or } \frac{\text{the calorific equivalent of hydrogen}}{\text{the chemical equivalent of zinc}} = 1060{\cdot}37\,;$$

consequently, x, the heat attendant on the oxidation of zinc, is thus obtained:—

Heat Units.

$$T = 567{\cdot}90$$
$$+b = 1060{\cdot}37$$
$$1628{\cdot}27$$
$$-a = 335{\cdot}54$$
$$x = 1292{\cdot}73$$

This number agrees very closely with the direct determination by Andrews and by Dulong, both of whom burned the metal in oxygen. The experiments of Andrews would give the number 1305, and those of Dulong 1304. But although the results agree very well in the present instance, the divergences are much greater in the case of iron and of copper.

The following are the results deduced by Favre and Silbermann, by operations conducted upon this principle; the quantities of heat evolved being calculated for 1 gramme of each element, when combined with a single *equivalent* (O=8) of the bodies with which it is united.

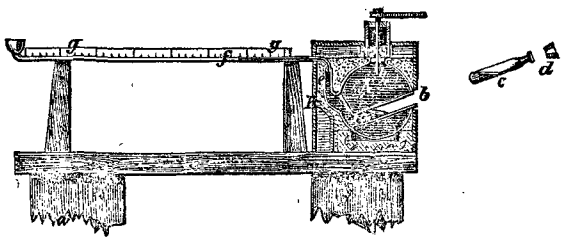
Elements.	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.
Hydrogen ...	34462	23783	9322	−3606	2741
Potassium ...		2587·7	2308	1977·2	1170·8
Sodium		4125·9			
Zinc	1291	1547·5			644·3
Iron	1352·6	1775·5			634·0
Copper	683·9	922·7			285·4
Lead	266·1	430·1	315·4	223·1	91·9
Silver	56·6	322·2	237·2	172·7	51·1

Notwithstanding the confidence with which these numbers are put forward by their authors, it must be admitted that the data necessary for the calculations by which they were obtained

are as yet very incomplete. The latent heat of oxygen in the gaseous state is unknown, and other important numbers are wanting: the results given in the foregoing table cannot, therefore, at present be received without great reserve.

(208) *Mercurial Calorimeter of Favre and Silbermann.*—Most of these experiments were performed by the aid of a *mercurial calorimeter* (*Ann. Chim. Phys.* 1852 [3], xxxvi. 33). This instrument may be regarded as a mercurial thermometer, with a very large bulb capable of receiving within it the substances which were submitted to experiment. It consists of a large iron or glass globe, A, fig. 159, of the capacity of about a litre, provided with

FIG. 159.



three apertures, one at the top and two at the sides. Into one of the lateral apertures, *b*, is fixed obliquely a tube of thin iron or of platinum, closed at the bottom; and into this tube, which is called the *muffle*, is introduced another tube, *c*, of very thin glass, containing the substances which are to be submitted to experiment: this glass tube is fitted into the metallic tube by means of a cork, *d*; a small quantity of mercury is placed within the muffle, the object of this expedient being to transmit the heat rapidly from the glass tube to the body of the calorimeter. The second lateral aperture, *e*, terminates in a neck which is curved vertically upwards, and into which is cemented the bent extremity of a horizontal capillary tube, *f*, of uniform bore, open at both ends, and of about 500 millimetres in length: by means of this tube the changes in volume of the mercury can be measured upon the scale, *g*, *g*. Through the upper aperture of the globe passes a steel piston, *h*, moved by a screw, by which means the column of mercury in the capillary tube can be reduced at pleasure to the zero of the scale. The globe is itself enclosed in a wooden case, *k*, lined with swan's-down in order to diminish the disturbing effects of external changes of temperature.

The value of the amount of expansion indicated was at once transformed into *units of heat*, by ascertaining the amount of ex-

pansion produced by the cooling of a given quantity of water from the boiling-point to a measured degree of temperature: by multiplying the number of grammes of water by the number of degrees Centigrade which it had lost in cooling, the number of *units of heat* was ascertained; since by our definition, a unit of heat is the quantity of heat required to raise 1 gramme of water 1° C. The number of millimetres by which the mercurial column had advanced in the capillary tube during the operation was next accurately measured; and by dividing this measured column by the number of heat units, the instrument was graduated so as to enable the observer to record at once the number of units of heat disengaged or absorbed during any chemical change.

This apparatus is excellent in principle, but it is open to certain objections in the mode of its construction:—the sides of the glass vessel are necessarily thick, to enable it to sustain the large weight of mercury with which it is filled; the glass, therefore, cannot rapidly and certainly adjust itself to the temperature of the hot mercury with which it is in contact. Moreover, the tubes are cemented into the three openings with mastic or marine glue. The apparatus to work well, should have been filled like a barometer or thermometer, since the presence of even a small bubble of air would materially affect the accuracy of the results. It is true that it is stated that the globe was filled with mercury *in vacuo*, but with cemented joints this precaution would soon be rendered useless. It is therefore necessary, in estimating the amount of confidence due to the results obtained by its use, to bear in mind these possible sources of inaccuracy. This is the more necessary, since it is principally in the numbers obtained by the use of this apparatus that the results of Favre and Silbermann differ from those of Andrews. At the same time it is to be remarked, that the results published by the French observers appear to be very consistent with each other.

(208 *a*) *Bunsen's Calorimeter.*—Bunsen has devised a very ingenious form of calorimeter, in which heat is measured by the amount of contraction which takes place during the liquefaction of ice (*Pogg. Ann.* 1870, cxli. 1). A cylindrical bulb of glass is blown, and in its axis a test tube, open at the top, is sealed. To the bottom of the cylinder a U tube is fused, and this latter communicates, by means of a cork, with a long horizontal capillary tube, graduated in millimetres. The lower part of the cylinder and the U tube contains boiled mercury, and the upper part of the cylinder is filled with water free from dissolved air. The whole apparatus except the capillary tube is surrounded with

snow or powdered ice, and a current of alcohol cooled in a freezing mixture is made to pass rapidly through the test tube (by fitting a cork with two tubes to the mouth of the tube); this causes a solidification of some of the water surrounding the test tube, and the cooling is continued until a considerable quantity of ice is formed. During the formation of the ice the increase of volume causes a depression of the mercury in the cylinder, and a corresponding movement of the mercury along the graduated tube. When the apparatus is to be used the alcohol is removed from the test tube, a plug of cotton wool attached to a platinum wire is passed to the bottom, and a small quantity of water introduced; the cylinder being kept in snow or powdered ice. When the column of mercury in the capillary tube has become stationary its position is noticed, and the body in which it is required to determine the amount of heat is dropped into the test tube on to the cotton wool, which thus prevents the fracture of the tube, and enables the operator to remove the substance more readily. The tube is then closed with a cork.

As the apparatus is not raised in temperature by the operation, there is no fear of loss of heat by radiation; hence one great source of the error in ordinary calorimeters is removed. The apparatus is also more delicate than any other hitherto described, as will be seen by the following experiment:—0·4 grm. of brass heated to 37° and plunged into 20 grammes of water at 0° C., raised the temperature, as indicated by a thermometer, 0·07° C.: but when placed in the calorimeter the mercury in the graduated tube was drawn back to the extent of 20^{mm}. This apparatus promises to be of great service in the determination of specific heats and for many other purposes.

(209) *On the Heat evolved during Metallic Precipitations.*—On the other hand, it must be stated that the varied and careful experiments of Andrews (*Phil. Trans.* 1848, 91) upon the heat evolved during the precipitation of several metals from their salts by the action of other metals, furnished numerical results differing from those calculated by Favre and Silbermann. In the experiments of Andrews, the corrections required are not in all cases completely under exact experimental control; in the displacement of copper by lead the correction amounts to one-eighth of the whole increment of heat, but in other instances the correction is trifling, not exceeding one-fiftieth of the amount of heat evolved; the numbers obtained are mutually consistent. An additional test of the accuracy of this method is afforded by the data furnished in two different series of experiments upon the amount of heat

obtained during the precipitation of copper by zinc—the corresponding numbers in both sets of experiments agreeing very closely with each other. In the first set of experiments metallic copper was precipitated from a strong solution of its sulphate by means of zinc, in a small glass vessel, and the heat estimated by the rise of temperature experienced by the water of a calorimeter in which the glass vessel was contained: in the second series, a dilute solution of sulphate of copper was employed, and the heat was measured by the rise in temperature experienced by the liquid itself. The mean of 4 experiments by the first plan gave 864 as the number of units of heat evolved by the precipitation of each gramme of copper from its sulphate; whilst the mean of 5 experiments upon the latter method was 868.

Table of Heat evolved during Metallic Precipitations.

Class of Salts used, and Metals employed for precipitating them.	Name of precipitated metal.	Units of heat evolved by precipitated metal.		Name of precipitating metal.	Units of heat for 1 gramme of precipitating metal.
		For 1 gramme	For 1 equivalent O=8.		
Salts of Copper by Zinc ...	Copper	868	27559	Zinc	847
Salts of Copper by Iron ...	Copper	592	18796	Iron	671
Salts of Copper by Lead ...	Copper	268	8509	Lead	82
Salts of Silver by Zinc ...	Silver	426	46007	Zinc	1416
Salts of Silver by Copper ...	Silver	161	17388	Copper	549
Salts of Lead by Zinc	Lead	182	18837	Zinc	580
Salts of Mercury by Zinc ...	Mercury	333	33300	Zinc	1025
Salts of Platinum by Zinc ...	Platinum	899	88552	Zinc	2724

The foregoing are the numbers given by Andrews, but he has purposely abstained from any attempt to deduce from them the amount of heat developed during the indirect oxidation of the metal which acts as the precipitant.

In these experiments a known quantity of finely-divided zinc, iron, lead, or copper, as the case might require, was mixed with a solution of the salt to be decomposed; taking care that the metal employed was always more than sufficient completely to decompose the salt in solution: the rise in temperature which occurred was noted with the usual precautions.

Andrews states, as the result of a large number of experiments, that the quantity of heat developed during the mutual action of the same pair of metals is the same, when an equivalent of one metal, A, displaces another metal, B, from any of its salts, whatever may be the acid of the salt employed, provided that B is in the same state of oxidation in each of the compounds submitted

to experiment. But if a different metal be employed to effect the precipitation, the amount of heat evolved is different. For instance, whether chloride, or sulphate, or acetate, or formiate of copper be precipitated by zinc, the quantity of heat developed in each case for every equivalent of copper is sensibly the same, viz., 27559. But if iron be substituted for zinc in the precipitation of the copper, the amount of heat is different, viz., 18796; though iron evolves the same amount of heat, whether the sulphate or the chloride of copper be employed. The principle, that the quantity of heat developed during the mutual action of the same pair of metals is always the same, whatever be the nature of the acid contained in the salts employed, has since been assumed by Favre and Silbermann in their calculations. If the metals be arranged in a list, beginning with those which develope the largest amount of heat when used as precipitants, the order in which they will stand is the following—zinc, iron, lead, copper, mercury, silver, and platinum. Now, it will be remarked that this is exactly in the electro-chemical order (261), zinc being the most electro-positive, and platinum the most electro-negative. Another interesting point of connexion between the thermal and the electrical phenomena exhibited by the metals is to be observed in the fact, that the nature of the acid contained in the salt which is undergoing decomposition does not influence either its thermal equivalent, or the electro-motive force (260) which it exerts when employed in the production of voltaic action.

The following remarkable conclusion was deduced by Andrews from these experiments:—If three metals, A, B, and C, be so related that A is capable of displacing B and C from their combinations, and B be also capable of displacing C, the heat developed by the substitution of A for C will be exactly equal to that developed in the substitution of A for B, together with that developed in the substitution of B for C:—

	Heat Units.
Thus 1 equivalent of lead displaced by zinc	= 18837
1 equivalent of copper by lead . .	= 8509
1 equivalent of copper by zinc . .	= 27346

The experimental number for copper by zinc being 27559

An analogous phenomenon is observed in the electrical relations of the metals (260): when three metals such as platinum, zinc, and potassium are arranged two and two in their electrical

order, the electro-motive force generated between the two extremes, platinum and potassium, is equal to the sum of the electro-motive forces of the pairs platinum and zinc, and zinc and potassium.

(210) *Calorific Equivalents of the Elements.*—The results obtained by the direct action of oxygen, chlorine, iodine, and bromine upon various elementary bodies, are summed up in the following Table, in which the numbers given indicate the quantity

Calorific Equivalents of various Elements (O=8).

Elements.	Observers.	Oxygen.	Chlorine.	Bromine.	Iodine.	Sulphur.
Hydrogen ...	F.S.	34462	23783	*9322	*−3606	*2741
Carbon	„	24240				
Sulphur	„	17760				
Phosphorus ...	A.	36072				
Potassium ...	A.		104476			
Ditto	F.S.		*100960	*90188	*77268	*45638
Sodium	„		94847			
Zinc	A.	42408	50659	41200	26670	
Ditto	F.S.	*42451	*50296			*20940
Iron	A.	33072	32696	23840	8636	
Ditto	F.S.	*37828	*49651			*17753
Tin	A.	33840	31843			
Arsenic	„		24992			
Antimony ...	Dulong.	30023	A. 30530			
Copper	„	19152	30495			
Ditto	F.S.	*21885	*29524			*9133
Lead	„	*27675	*44730	*32802	*23208	*9556
Silver	„	*6113	*34800	*25618	*18651	*5524

of heat evolved by the union of equivalent quantities of oxygen, chlorine, iodine, and bromine, with each element, taking as the standard of comparison the number of grammes of water at 0° C., which would be raised to 1° C. by the combustion of 1 gramme of hydrogen in oxygen. In this case the numbers for the different elements are all calculated from their equivalent numbers, not from the atomic weights. The quantities of heat thus given out are termed by Favre and Silbermann the *calorific equivalents* of the different elements.

The numbers to which an A. is prefixed are those of Andrews: F. S. indicate those of Favre and Silbermann: when an asterisk is prefixed to any number, the result has been calculated by indirect methods, upon the principle already explained (207).

From an examination of the foregoing Table of calorific equivalents, it will be obvious that the quantity of heat evolved in the act of combination is greatest in those cases in which the chemical attraction between the two elements is the strongest, and where

the compound possesses the greatest stability. No definite quantitative expression of the law which regulates the evolution of heat during combination, can, however, be deduced from these numbers, owing to the variety of disturbing causes when bodies are compared in the solid state.

(211) *On the Heat developed during the Reaction of Acids upon Bases.*—A careful and extensive series of experiments upon the heat developed during the saturation of dilute solutions of different acids, by each of the more important bases with which they form soluble compounds, was published by Andrews in 1841 (*Trans. Roy. Irish Acad.*, xix. 228). In these experiments a slight excess of acid was purposely employed; the bases, where it was possible, being in a state of solution. When the bases are in the insoluble form, the heat observed is of course lower than that due to the chemical action; a portion being absorbed in the passage of the base from the solid to the liquid condition; but although the quantity of heat so absorbed is unknown, this amount is constant for the same base, and therefore the observed results obtained for the combination of equal quantities of this base with different acids are mutually comparable.

Heat Units evolved by the Action of 1 *Equivalent of*

	ANDREWS.									FAVRE.	
Acids.	Potash.	Soda.	Baryta.	Ammonia.	Magnesia.	Lime.	Zincic Oxide.	Plumbic Oxide.	Argentic Oxide.	Potash.	Soda.
Sulphuric ...	16700	16600	...	14700	18400	...	12000	...	...	16083	15810
Sulphurous	16300	...	...	...	...	...	...	...	...	...	...
Nitric.... ...	14800	14500	15300	12700	17600	15800	10600	9300	7200	15510	15283
Phosphoric	14700	14300	15200	...	...	...	...	...	..	17766	...
Arsenic	14700	14400	...	12600	...	...	...	...	...	...	...
Hydrochloric	14900	14700	...	12900	17600	15600	10800	...	...	15656	15128
Hydrobromic	...	...	...	...	...	...	...	...	...	15510	15159
Hydriodic ...	15000	14700	15500	12400	...	...	10200	...	...	15698	15097
Chromic.....	14400	...	...	...	...	...	...	...	...	...	...
Oxalic	15100	15000	...	13100	...	...	...	...	...	14156	13752
Acetic	13800	14000	14300	12300	...	15500	...	8400	...	13973	13600
Formic	14200	...	...	...	...	...	...	...	...	...	13308
Tartaric.....	13500	13400	...	11700	...	...	...	...	...	13425	12651
Citric	13600	13200	...	11400	...	...	...	...	...	13658	13178
Succinic.....	13600	13200	...	11400	...	...	...	...	...	...	...

* In the Table, showing the heat units evolved in the action of the acids on bases, the results obtained by Dr. Andrews from a later series of experiments, which were communicated in 1870 to the Royal Society of Edinburgh, are substituted for those given formerly in this work. The new results comprise the heat evolved in the action of potash, soda, and ammonia on sulphuric, nitric, hydrochloric, oxalic, acetic, and tartaric acids. In the

A *résumé* of this subject is given by the same author in a "Report on the Heat of Combination," published in the *Report of the British Association* for 1849, 69. From these experiments it appears:—

1. "That an equivalent of the same base, combined with different acids, produces *nearly* the same quantity of heat.

2. "An equivalent of the same acid, combined with different bases, produces different amounts of heat.

3. "When a neutral salt is converted into an acid salt by combining with one or more equivalents of an acid, no disengagement of heat occurs.

4. "When a double salt is formed by the union of two neutral salts, no disengagement of heat occurs.

5. "When a neutral salt is converted into a basic salt, the combination is accompanied by the disengagement of heat.

6. "When one and the same base displaces another from any of its neutral combinations, the heat evolved or absorbed is always [nearly] the same, whatever the acid element may be."*

The results of Favre and Silbermann lead to conclusions sub-

the Undermentioned Bases on 1 *Equivalent of certain Acids.*

AND SILBERMANN.

Baryta.	Ammonia.	Magnesia.	Lime.	Zincic Oxide.	Manganous Oxide.	Nickelous Oxide.	Cobaltous Oxide.	Ferrous Oxide.	Cadmic Oxide.	Cupric Oxide.	Plumbic Oxide.	Argentic Oxide.
...	14690	14440	...	10455	12075	11932	11780	10872	10240	7720	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
15360	13676	12840	16943	8323	10850	10450	9956	9648	8116	6400	9240	6206
...	...	..	...	...	...	...	...	...	..	...	...	...
...	...	...	..	...	...	...	...	...	...	...	...	...
...	13536	13220	...	8307	11235	10412	10374	9828	8109	6416	...	..
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	..	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	..	...	...	...
...	12649	12270	...	7720	9982	9245	9272	8590	7546	5264	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...

other cases, the numbers have been calculated from his earlier experiments, which were communicated in 1841 to the Royal Irish Academy, no correction has been made, as was attempted in former editions, for the specific heat of the solutions employed, as the data for making these corrections are very imperfect, and they have not been made by Dr. Andrews himself in either of his original papers.

stantially similar, though the absolute quantities of heat which they obtained, in many cases differ considerably from those published by Andrews. The table which is given at the bottom of the two preceding pages indicates the amount of heat obtained by both observers by acting on 1 equivalent of each of the different bases with each acid, the acid being always very slightly in excess.

In the present stage of our knowledge upon this subject, it appears safest to state, that the quantity of heat emitted during the act of combination of equivalent quantities of different acids with a given base, although nearly the same, is not rigidly so. They might probably be arranged in *isothermic* groups, as follows, —those which stand first evolving most heat:—

	With 1 Eqt. of Potash.
1. Sulphuric and sulphurous acids . . .	16700—16300
2. Oxalic, nitric, phosphoric, arsenic, hydrochloric, hydriodic	15100—14700
3. Chromic, formic, acetic	14400—13800
4. Tartaric, citric, succinic	13600—13500

The bases also differ in the amounts of heat which they evolve in acting on the same acid; but as only a very few of the bases are soluble in water, their thermic powers cannot be compared in so simple a manner as those of the acids. Potash, soda, and baryta seem to be nearly isothermic, whilst ammonia is decidedly inferior to these bases. Lime, magnesia, and the other insoluble oxides cannot be satisfactorily compared with each other, until the amount of heat which is absorbed during their passage into the liquid form is known.

(212) *Estimate of Heat absorbed during Solution of Salts.*— During the solution of saline bodies in water, heat is generally absorbed; but in a few instances where anhydrous salts are dissolved, as in the case of the chlorides of zinc, iron, and copper, an evolution of heat occurs, owing to the preliminary formation of a solid hydrate. The following are experimental data furnished by Favre and Silbermann upon this point (*Ann. Chim. Phys.* 1853 [3], xxxvii. 414). The presence of very different quantities of water of crystallization in the various salts furnishes a partial explanation of the fact, that no relation is observed between the quantities of heat absorbed during the solution of the molecule of each compound:—

Heat Absorbed during the Solution of Salts.

Name of Salt.		Molecular weights.	Heat units absorbed by 1 gramme.	Heat absorbed by 1 mol. in grammes.
Potassic sulphate	K_2SO_4	174·2	35·3	6149
Sodic „	$Na_2SO_4,10H_2O$	322	49·1	15810
Ammonic „	$(NH_4)_2SO_4$	132	11·1	1465
Zincic „	$ZnSO_4,7H_2O$	287	14·8	4248
Ferrous „	$FeSO_4,7H_2O$	278	12·1	3442
Potash-alum	$K_2Al_2(SO_4)_4,24H_2O$	949·2	23·1	21928
Ammonia-alum	$(NH_4)_2Al_2(SO_4)_4,24H_2O$	907	19·0	17232
Hydric potassic sulphate	$KHSO_4$	136·1	25·6	3484
Potassic chloride	KCl	74·6	51·9	3872
Sodic „	NaCl	58·5	8·9	521
Ammonic „	NH_4Cl	53·5	65·1	3483
Calcic „	$CaCl_2,6H_2O$	219	15·5	3394
Strontic „	$SrCl_2,3H_2O$	212·6	24·9	5294
Baric „	$BaCl_2,2H_2O$	244	16·9	4124
Potassic bromide	KBr	119·1	37·8	4502
Potassic iodide	KI	166·1	29·2	4850
Potassic nitrate	KNO_3	101·1	70·5	7127
Sodic „	$NaNO_3$	85	45·5	3867
Ammonic „	NH_4NO_3	80	65·9	5272
Calcic „	$Ca(NO_3)_2,4H_2O$	236	27·1	6396
Strontic „	$Sr(NO_3)_2,4H_2O$	283·6	41·2	11685
Plumbic „	$Pb(NO_3)_2$	331	14·9	4932
Argentic „	$AgNO_3$	170	31·1	5287

(213) *Heat evolved during the Solution of Gases.*—During the solution of gases in water, a considerable evolution of heat takes place, which has been estimated by Favre and Silbermann in the following instances (*Ann. Chim. Phys.* 1853 [3], xxxvii. 410).

Name of Gas.	Formula.	Atomic weights.	Heat units from 1 gramme.	Heat units from 1 eqt. in grammes.
Sulphurous anhydride	SO_2	64	120·4	7706
Hydrochloric acid	HCl	36·5	449·6	16410
Hydrobromic acid	HBr	81	235 6	19084
Hydriodic acid	HI	128	147·7	18905
Ammonia	H_3N	17	514·3	8743

CHAPTER VI.

MAGNETISM AND ELECTRICITY.

I. *Magnetism*.—II. *Static Electricity*.—III. *Dynamic or Voltaic Electricity*.—IV. *Electro-Magnetism*.—V. *Magneto-Electricity*.—VI. *Thermo-Electricity*.—VII. *Animal Electricity*.—VIII. *Diamagnetism*.

(214) Magnetism and electricity are now found to be so intimately related, that it is hardly possible to study the operations of either separately.

The property of the loadstone to attract small pieces of iron was recognized as a remarkable natural phenomenon for centuries before the Christian era; and the 'pointing' of the magnetic needle north and south, was early applied to the purposes of navigation by the Chinese; but it was not employed for that purpose by European nations till the latter end of the fifteenth century. The property of temporarily attracting light objects, which amber acquires when rubbed, was also familiar to the Grecian philosophers; but it was not till about 280 years ago that Gilbert laid the foundation of electrical science, and that Otto de Guericke and Hauksbee contrived the first electrical machines. Nautical men, likewise, had often observed that after a ship had experienced a stroke of lightning, the compass was deranged or its poles were reversed; but it was not until the year 1819 that the true connexion between electricity and magnetism was pointed out by Oersted, when he published his memorable discovery, that a magnetic needle, if suspended freely at its centre, would place itself at right angles to a wire which was transmitting an electric current. After the publication of Oersted's discovery, the means of obtaining powerful temporary magnets by transmitting electrical currents through wires coiled round masses of soft iron, or in other words, the methods of preparing electro-magnets, were speedily devised; and thus the dependence of magnetism on electricity in motion was shown: whilst in 1831 the completion of this chain of discovery was effected by Faraday, who announced that a current of electricity might be obtained in a closed conducting wire from the magnet, by moving it across the line of the conductor.

In its chemical bearings, particular importance is attached to Volta's invention of the voltaic pile or battery, which, in the hands of Davy, led to the discovery of the metallic bases of the

alkalies and of the earths, and effected a complete change in the aspect of chemical science. In later years, the applications of the voltaic battery to the chemical arts of gilding, silvering, zincing, &c., have rendered it an instrument of great importance in the industrial arts.

§ I. Magnetism.

(215) It will not be necessary to enter fully into the subject of magnetism, but a few remarks upon its more important peculiarities will materially aid in fixing upon the mind clear ideas of polarity and attraction.

Electricity is, like magnetism, polar, and the phenomena of chemical attraction also fall into the class of polar actions.

The most obvious character of magnetism is seen in the power of attracting masses of iron, which is displayed to a greater or less extent by magnetized bodies. This property of attracting iron was first observed by the ancients in an iron ore obtained from Magnesia, in Asia Minor: hence the property was termed *magnetism*, and when in more recent times its directive property was observed, the mineral itself was named the *lead-stone* or loadstone. A steel bar if rubbed in one direction with the loadstone acquires similar properties; when poised horizontally, as may be done by supporting it upon a point, such a bar will take up a fixed position with regard to the poles of the earth; in this country it will point nearly north and south. The end of a magnetic bar which points towards the north is distinguished by a mark, and is hence often termed the *marked end* of the magnet. This peculiarity in the magnet of taking a fixed direction, renders it invaluable to the navigator. A magnetized needle attached to a card marked with the cardinal points, and properly poised, constitutes the *mariner's compass*.

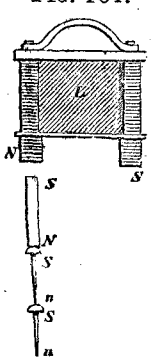
If a sheet of paper be laid over a magnetized steel bar, and iron filings be evenly sifted upon the paper, it will be found, on gently tapping the paper, that the particles of iron accumulate in two groups, one around each extremity of the bar, and that from these poles the filings arrange themselves in curved lines, somewhat resembling those shown in fig. 160, extending from one end of the bar to the other. This experiment shows that the attractions are concentrated near the two extremities of such a bar. A soft iron wire freely

Fig. 160.

suspended at its centre, in a horizontal direction, will be attracted indifferently at both ends by either end of the magnetic bar; but if a second magnetic bar be poised in the same way as the iron wire, it will be found that one end of this bar will be attracted when the magnet is brought near it in one direction, whilst the same end will be repelled if the opposite end of the magnet be presented to it. Further examination shows that this repulsion takes place when the ends presented to each other are those which would naturally point in the same direction; two north ends repel each other, and similar repulsion ensues when two south ends are presented to each other; whereas, if the extremities presented naturally point in opposite directions, attraction ensues between them: the north end of one bar attracts the south end of the other. Hence it appears that there are two kinds of magnetism, endowed with qualities analogous, but opposite to each other. The two kinds are always developed simultaneously, are always equal in amount, but are opposite in their tendencies; and thus are capable of exactly neutralising each other. They accumulate at opposite ends of the bar. These ends are termed the *poles* of the magnet.

(216) *Magnetic Induction.*—Magnetism acts through considerable intervals of non-magnetic matter upon bodies such as iron, which are susceptible of magnetism, and it produces a temporary development of magnetism in such magnetizable substances. A piece of soft iron brought near to a magnet immediately assumes the magnetic state. This influence of the magnet operating at a distance is termed *magnetic induction*, and it is in consequence of this action that the iron is attracted. If the north end, N, of a magnet, L (fig. 161), be presented to a piece of soft iron, the latter becomes a magnet with its poles similarly arranged; that is to say, the soft iron acquires in the extremity, s, presented to the permanent magnet, magnetism of the opposite kind to that of the end, N, of the magnet, L, which it is made to approach. The soft iron will now attract other pieces of iron, *s n*, *s n*, and they in turn will act upon others, by a continuation of the induction. On gradually removing the permanent magnet, the effects diminish as the distance increases, and at length disappear altogether. This diminution in the effect takes place much more rapidly than in the ratio of the squares of the distance from the magnetic pole, but the exact law has not as yet

FIG. 161.



been calculated. The polar character of magnetic induction may be seen by suspending two pieces of soft iron wire over one of the poles of a magnet, s (fig. 162); the lower ends of the wires *n*, *n*, repel each other, but are both drawn towards the magnet, and the upper extremities, *s*, *s*, also repel each other. It is this mutual repulsion of the corresponding ends of the pieces of iron which causes the iron filings (fig. 160) to distribute themselves in curves around the magnet; for in this experiment each particle of iron becomes for the time a magnet with opposite poles. It is likewise in consequence of this polarity that a number of pieces of fine iron wire under induction form a continuous chain. A bar of soft iron placed on a magnet of equal dimensions neutralizes its action for the time: by connecting the two extremities of the magnet, it diverts the induction from surrounding bodies, and concentrates it upon itself. On the other hand the induction is much strengthened if the magnetic circle be completed, as in fig. 163, by uniting the pieces of iron suspended from either pole by the connecting piece, *a b*. This induction is maintained across the greater number of bodies, such as atmospheric air, glass, wood, and the metals. It is, however, modified by the interposition of iron, cobalt, and nickel, which are themselves powerfully susceptible of magnetism.

FIG. 162.

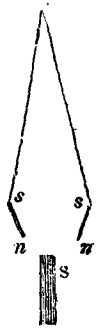
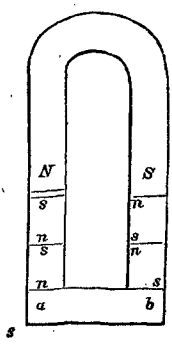


FIG. 163.



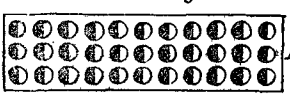
Magnetic induction differs essentially from electric induction (228) in this particular—viz., that it is not possible to insulate either kind of magnetism from the other. For instance, if one end of the two united pieces of iron, *s n*, *s n* (fig. 163), exhibit the properties of a north magnetic pole, the other end will exhibit those of a south magnetic pole; but if the two pieces of iron, whilst still under the influence of induction, be separated from each other, and then the magnet be withdrawn, both pieces of iron will have lost their magnetism. Again, if a magnet be broken in the middle, it will not be separated into one piece with a north and another with a south pole; each fragment will still possess two poles, turned in the same direction as those of the original bar (fig. 164); and each fragment may again be subdivided into an indefinite number of smaller

FIG. 164.

fragments, each of which will still possess a north and a south pole.

These phenomena may be explained by supposing that a magnet consists of a collection of particles, each of which is magnetic and endued with both kinds of magnetism. In the unmagnetized condition of the bar, these two kinds of magnetism are mutually combined, and exactly neutralize each other; but when the mass becomes magnetized, the two kinds of magnetism are separated from each other, though without quitting the particle with which they were originally associated. The two halves of each particle assume an opposite magnetic condition. All the north poles are disposed in one direction; whilst all the south poles are disposed in the opposite direction. Each particle thus acquires a polar condition, and adds its induction to that of all the others: as a necessary consequence of such an arrangement, the opposite kinds of magnetism become accumulated at the opposite extremities of the bar. If in fig. 165 the small circles be taken to represent the ultimate magnetic particles, the portions in shadow would indicate the distribution of south magnetism, while the unshaded half of the particles would show the distribution of magnetism of the opposite kind. This hypothesis is supported by the fact that a magnet whilst producing induction loses none of its strength, but on the contrary suffers temporary increase of strength, owing to the reaction of the induced magnetism of the soft iron upon it.

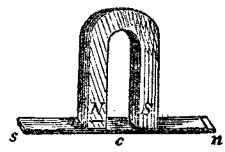
FIG. 165.



(217) *Preparation of Magnets.*—Pure soft iron loses its magnetism as soon as it is withdrawn from the inductive influence; but the presence of certain foreign bodies in combination with the iron, particularly of oxygen, as in the natural loadstone, and of carbon, as in steel, enables the body to retain the magnetization permanently. Hardened steel is always the material employed in the preparation of permanent magnets; it is not susceptible of so intense a degree of magnetization as soft iron, but when induction has once been produced within it, the effect is retained for an indefinite length of time. The development of this power in steel is much facilitated by friction; and the amount of force developed by this means is greatly dependent upon the direction in which the friction is performed. A simple method of magnetizing a bar consists in placing the bar on its side and bringing down upon one of its extremities either of the ends of a bar magnet. If the north end be brought down on the steel bar, it must be drawn

slowly along towards that end of the bar which it is intended shall possess south polarity: this operation must be repeated three or four times in the same direction. A more effectual plan is to bring down upon the centre of the bar the two ends of a powerful horseshoe magnet as represented in fig. 166; the south pole being directed towards the end of the bar that is intended to possess the northern polarity, and *vice versâ*. It is then moved along the surface from the middle, alternately towards either end, taking care not to carry the horseshoe beyond the ends of the bar, and to withdraw the horseshoe from the bar when at its centre, *c*. The bar is then turned over and the process repeated on the opposite side, but in the same direction, for an equal number of times. When two bars are to be magnetized, they may be placed parallel to each other, the ends being connected by pieces of soft iron. Both the poles of the horseshoe are brought down upon the centre of one of the steel bars, and it is carried round the parallelogram always in the same direction, taking care, as before, to withdraw it when over the centre of one of the bars. In the last arrangement, the induction of one bar acts upon and increases the intensity of the magnetism excited in the other. For this reason, the opposite poles of magnets, when not in use, should be connected by pieces of soft iron, so that the continued induction shall maintain the magnetism of each.

Fig. 166.



In the act of magnetization, the horseshoe loses nothing of its power, but the north and south magnetism, which are supposed to exist in every particle of steel and iron, and which in the unmagnetized condition are so combined as exactly to neutralize each other, appear from the effect of the induction to which they have been subjected, to be permanently disturbed in their equilibrium in the newly-magnetized bars. The more intense the power of the horseshoe, the greater is this disturbance, and the more powerful are the magnets which are produced.

By uniting together several bar magnets, taking care that the corresponding poles of each are in the same direction, *magnetic batteries* of great power may be obtained. The magnets should be all as nearly as possible of the same strength; because if one of the bars be weaker than the others, it materially diminishes the power of the whole, and acts in the same manner as a bar of soft iron would do, although to a more limited extent. M. Jamin has recently constructed magnets of great power by uniting into one

horseshoe a considerable number of thin magnetized steel strips. As a matter of convenience, the bar magnet is often bent into the form of a horseshoe, so that the induction and attraction of both poles may be simultaneously exerted on the same piece of iron: the effect is in this manner much increased, and the weight sustained by the two poles united is much greater than the sum of the two weights which would be supported by each pole separately. For this reason, the soft iron armatures N, S, of a loadstone (fig. 161) add greatly to its strength, and by facilitating the application of the *keeper*, or piece of soft iron which connects the two poles when not in use, prevent the loss of the magnetic power.

(218) *Influence of Molecular Motions on Magnetism.*—It has been mentioned that the friction of a steel bar, whilst under induction, facilitates its magnetization. The same effect is occasioned by percussion of the bar, or by any other mode of producing vibration in it whilst it is under magnetic induction. On the other hand, if a bar has been fully magnetized, its strength is reduced by the application of a sudden blow; even the simple act of scratching the surface with sand-paper, or with a file, may seriously impair the strength of a good magnet.

The influence of heat on magnetism is remarkable. If a steel bar be ignited and placed under induction, and whilst still in this condition it be suddenly quenched, it will be found to be powerfully magnetic. Again, if a steel magnet be ignited, and allowed to cool slowly, all its acquired magnetism will have disappeared. Elevation of temperature, therefore, evidently favours the transfer of magnetic polarity within its particles. Further, if the temperature of a piece of iron be raised to redness, about 980° (527° C.), it will become indifferent to the presence of a magnetic needle, although on again cooling it will be as active as before. A similar effect is produced upon cobalt at the temperature of melting copper.* Nickel at a much lower temperature loses its action upon the magnet, as at 600° (316° C.) it exerts scarcely any attraction on the needle. So great is the influence of temperature upon a magnetic bar, that at the boiling-point of water, the diminution of its strength is perceptible by the rudest tests. If the temperature do not exceed the boiling-point of water, the magnet regains its strength on cooling. On the other hand,

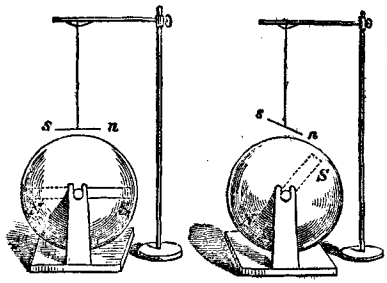
* Faraday has, however, shown that in the case of cobalt its magnetic power increases as the temperature rises until it reaches about 300° (149° C.), beyond which it slowly diminishes, and at length becomes nearly evanescent. (*Phil. Trans.* 1856, 179.)

by cooling a magnet artificially, its strength is for the time exalted.

(219) *Measurement of Magnetic Strength of a Bar.*—The simplest method of ascertaining the strength of a magnet, consists in attaching to its armature a scale-pan, and ascertaining the weight which it will support; but it is obvious that this plan is not susceptible of any high degree of accuracy; it is, moreover, in many cases, quite inapplicable. A still easier, and more generally useful, because far more accurate, method, consists in suspending the magnet horizontally at its centre, by means of a few fibres of silk, and allowing it to take a fixed direction under the influence of a standard bar magnet, sufficiently long to be considered as acting by a single pole only upon the magnet under experiment: it is then displaced from its position of equilibrium, and the number of oscillations which it describes in a given time is counted. The relative magnitude of the strength of two or more equal bars, which may thus be compared, is proportionate to the square of the number of vibrations performed in equal intervals of time, when the two bars are placed at the same distance from the standard magnet. For estimating low degrees of power, the torsion of a glass thread, as employed in Coulomb's electrometer (226), may be used.

(220) *Magnetism of the Earth—The Dip.*—The remarkable fact of the pointing of the needle towards the north pole of the earth has been explained upon the hypothesis that the globe of the earth itself is a magnet, the poles of which are situated nearly in the line of the axis of rotation; the magnetism of the earth's north pole being of the same kind as that of the unmarked end of the magnet. If a small magnetized needle, *s n*, be freely suspended horizontally by a thread over the equator of a sphere (fig. 167) 9 or 10 inches (about 25 centimetres) in diameter, in the axis of which a small magnetic bar, N S, at right angles to the axis of suspension of the globe, is placed, the needle will, when the magnetic bar is horizontal, as in No. 1, assume a direction parallel to the magnetic bar, and will point towards N and S, preserving its horizontal position; for it is equally attracted by the north and south polarities of the bar; but if one of the ends of the magnetic bar be made gradually to approach the needle as at 2,

FIG. 167.



that end of the needle which previously pointed towards this pole will begin to incline downwards, or to *dip*, until when the ends of the bar is exactly under the point *n* of the needle, the direction of the needle will become vertical. On bringing the opposite end of the bar towards the needle, like results may be obtained with the other end of the needle. Similar phenomena are also exhibited when a magnetic needle, poised horizontally at the equator of the earth, is carried towards either of its poles. A needle, therefore, which when unmagnetized is so poised as to assume a horizontal position, in the latitude of London, appears to become heavier at its marked end by the process of magnetization. An instrument by means of which the angular amount of this *inclination* can be accurately observed, is called a *dipping-needle*.

(221) *Declination or Variation.*—In each hemisphere there is a single point at which the dipping-needle stands vertically, *i.e.*, where the dip is 90°. In the northern hemisphere this point was found in 1831 by Sir James Ross, situated in 96° 46′ W. lon. and 70° 5′ N. lat.; the point where it would be vertical in the southern hemisphere being nearly in 75° S. lat. and 138° E. lon. *The line of no dip* does not coincide with the earth's equator; it forms an irregular curve inclined to it at about 12°, and crossing it in four places. This arises from the fact that the magnetic system of the earth is much more complicated than is represented in the foregoing paragraph. Instead of being single, it appears to be *double*, as was first pointed out by Halley, and in neither of these two systems does the magnetic axis coincide with the axis of rotation of the earth. Consequently in most places the needle does not point to the true geographical north. At the present time the needle in London points rather less than 19½° west of north. This deviation from the true north is termed the *variation* or *declination* of the needle.

In the northern hemisphere there are two lines of no declination, which pass through the point of 90° of dip, and a closed curve including part of Siberia and China. These lines of no declination have reference to a double magnetic system of which the two points of maximum force in the northern hemisphere are resultants; and these points were called by Halley *magnetic poles*. They do not correspond to either of the points of 90° of dip, which have also been called magnetic poles.

It is remarkable that the declination of the magnetic needle is not constant at the same spot. In the year 1657, the needle, pointed due north at London. It then gradually assumed a decli-

nation to the west, which continued to increase until about the year 1840, at which time the variation to the west, in London, was nearly 25°; since this period it has been gradually returning towards the east, and on January 1, 1867, it was 20° 52′ W. at Kew. The rate of its motion differs in different parts of its progress, becoming slower as it approaches the point of retrogression; at present it is about 8′ annually. Independently of these gradual and progressive changes, the variation is subject to diurnal movements of very small amount: north of the magnetic equator in England and the middle latitudes, the north end of the needle moves slowly eastward in the forenoon, attaining its maximum between the hours of seven and ten A.M., and returns to its mean position at about ten in the evening. Connected with these alterations are corresponding variations in the dip, which during the last fifty years has been observed in London to diminish annually about 2′·6 From observations made at the Kew Observatory, the dip, in January, 1867, was 68° 5′.

The following table, kindly supplied by Mr. G. M. Whipple, the superintendent of the Kew Observatory, shows the changes of the mean values of the declination and dip which have taken place since 1868:—

Year.	Declination West.	Inclination.
1868	20° 33′ 9″	68° 2′ 6″
1869	20 25 52	68 1 6
1870	20 19 13	67 58 30
1871	20 10 32	67 56 43
1872	20 0 31	67 54 9
1873	19 57 44	67 51 53
1874	19 51 58	67 50 1
1875	19 41 14	67 48 28
1876	19 31 53	67 46 44
Month. January } 1877	19 24 6	67 46 9

The total diminution of declination from 1868 to 1876 is therefore 1° 1′ 16″, the yearly average being 7′ 39″·5, and of inclination 15′ 22″, or 1′ 55″·25 per year on the average.

(222) *Variation in the Intensity of the Earth's Magnetism.*—The *intensity* of the earth's magnetism is also found to vary at different points of the surface, but the law of its increase has not been clearly determined; the line of minimum intensity, or *magnetic equator*, as it is sometimes called, is in the vicinity of the geographical equator, but does not coincide either with this or with the line of no dip: it forms an irregular curve cutting both of these lines. The points of greatest intensity, moreover, do not coincide with those at which the dipping-needle is vertical. The

highest degree of intensity that has been actually measured is 2·052, the lowest 0·706.* Both the maximum and minimum here mentioned are in the southern hemisphere. If it be supposed that the globe be divided by a plane passing through the meridians of 100° and 260°, the western hemisphere, comprising America and the Pacific Ocean, presents a higher intensity than the eastern; but the charge of the northern and of the southern hemisphere is equal. In the northern hemisphere there are two points of maximum intensity, the most powerful being in North America, and determined by Lefroy, in 1843-44, to be situated in 52° 19′ N. lat: 92° W. lon., the intensity being 1·88. The weaker maximum was found by Hansteen in 1828-29 in Siberia, in 120° E. lon. with an intensity of 1·76. Sir James Ross in 1842-43, found the principal maximum in the southern hemisphere in about the meridian of 134° E. and a few degrees North of the Antarctic circle, whilst the weaker maximum in the southern hemisphere, according to Sabine, is about 130° W. The intensity of the magnetic force at London is now 1·372.

The intensity of the earth's magnetism, like the variation and the dip, is found to suffer periodical changes. Besides these regular variations of the magnetism of the earth, other irregular variations have been observed. These have been termed *magnetic storms:* they are indicated by sudden and considerable disturbances of the magnetic instruments, of short duration, which are produced by some widely acting causes, as these disturbances have been noticed simultaneously at very distant parts of the earth's surface. In extreme cases, the diminution of the magnetic intensity during the 'storms' has amounted to a large portion of its total intensity. Sabine considers that these magnetic storms are connected with changes in the solar atmosphere, which are indicated by variations in the number and form of the spots upon the sun's disk; their epochs of maximum recurring at intervals of 11·11 years, with epochs of minimum intensity occurring midway between each pair of maxima. These intervals coincide

* The unit of intensity used in the text is that proposed by Humboldt, derived from the value of a particular magnet which he employed; but in the later magnetic observations the unit of intensity employed has been that recommended by the Royal Society, viz.: a second of time, a foot of length, and a grain of mass. The magnetic intensity upon this scale at London was, in January, 1867, 10·301; and in January 1877, 10·2809: the horizontal force being at the latter date 3·8896. The two last numbers expressed in the centimetre-gramme-second system of units will be ·4740 and ·1793 respectively.

with the 11·11-year epochs of maximum and minimum of the solar spots observed by Schwabe.*

Since, then, the earth may be looked upon as an immense magnet of small intensity, it is natural to expect that, under favourable circumstances, magnetic induction should arise from its influence. Such effects are indeed continually observed. If a soft iron bar be placed in the line of the dip, it acquires temporary magnetic properties, the lower extremity in the northern magnetic hemisphere acting as the marked pole of a magnet upon a magnetized needle, while the upper extremity acts as the unmarked pole. By reversing the position of the bar, the end which is now the lower will still possess the magnetism of the marked pole. A bar of steel which is kept in a vertical position (a line in this latitude not far removed from that of the dip), is from this cause frequently found to be permanently, though weakly, magnetic. It is to the same cause operating through the lapse of ages, in the same direction, upon the loadstone, that its polarity is to be ascribed.

If a steel bar be made to vibrate while placed in the line of the dip, as by giving it a smart blow, it is magnetized still more powerfully, and this effect may be still further increased by the induction of other masses of iron placed in contact with it. For instance, by allowing a steel bar, supported in the line of the dip, to rest upon an anvil, and striking it strongly with a hammer, it becomes decidedly magnetized. All permanent magnetism may, however, again be removed from it by placing it *across* the line of dip, and striking it two or three blows as before.

Iron, nickel, and cobalt are the only substances which are powerfully magnetizable; but a susceptibility to magnetism in a much feebler degree has, by the researches of Faraday and others (323), been proved to exist in a variety of other bodies. Before describing the method in which these experiments were conducted, it will be necessary to examine the leading phenomena of electricity; and these will now be considered.

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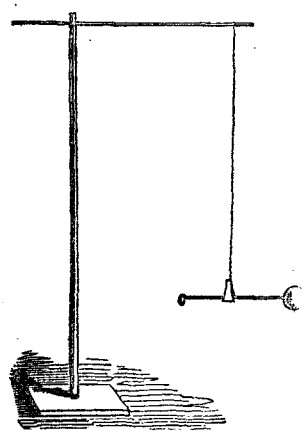
* A singular corroboration of this theory is afforded by an observation of Mr. Carrington, who was watching a large spot on the sun on 1st September, 1859: suddenly, at $11^{h}\cdot 20$ min. A.M., a bright spot was seen in the middle of the dark one; this appearance lasted for about ten minutes, and a corresponding disturbance in time and duration was indicated by the self-registering magnetometers at Kew. Brilliant auroræ were simultaneously observed in various parts of the world.

§ II. Statiç Electricity.

(223) Electricity is one of those subtle and all-pervading influences which are intimately connected with the operations of chemical attraction. Indeed some eminent philosophers have been disposed to regard electricity and chemical attraction in the light of different manifestations of the same cause.

For upwards of 2000 years it has been known that when amber is rubbed upon bodies such as fur, or wool, or silk, it acquires for a short time the property first of attracting light objects, such as fragments of paper or particles of bran, and afterwards of repelling them. Until about 280 years ago, amber was the only known substance by which such effects were produced. About that time Gilbert discovered that a number of other bodies, such as glass, sealing-wax, and sulphur might be made to excite similar motions. The power thus called into action has been called *electricity*, from ἤλεκτρον (amber), the body in which it was first observed. Independently of its origin in friction, it has been found that electricity is liberated by chemical action, by certain vital operations, by heat, by magnetism, by compression, and in fact by almost every motion that occurs upon the face of the globe. Electricity neither increases nor diminishes the weight of bodies under its influence, and neither enlarges nor reduces their volume. It may be excited in all substances, may be communicated from one electrified or *excited* body to another previously in a *neutral* or unelectrified condition, and it may be stored up for the purposes of experiment.

Fig. 168.



(224) *Two kinds of Electricity.*—A very simple contrivance will suffice for examining the fundamental phenomena of electricity as developed by friction:—

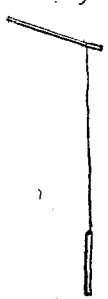
Soften a little sealing-wax in the flame of a candle, and draw it out into a thread 8 or 10 inches (20 or 25 centimetres) long, and of the thickness of a stout knitting pin. Attach to one end of it a disk of paper about an inch in diameter, as represented in fig. 168; suspend this rod and disk by means of a paper stirrup and a few fibres of unspun silk from a glass rod fixed horizontally to some convenient support. Now rub a stick of

sealing-wax with a bit of dry flannel, and bring it near the paper disk; the disk will at first be strongly attracted, and will then be as strongly driven away. Whilst it is in this condition of repulsion by the wax, bring towards it a warm glass tube that has been rubbed with a dry silk handkerchief; the disk will be immediately attracted, and in an instant afterwards it will again be repelled, but it will now be found to be attracted by the wax. It is therefore evident, that by the friction of the glass and of the wax, two similar but opposite powers are developed. A body which has been electrified or *charged* with electricity from the wax is repelled by the wax, but it is attracted by the excited glass, and *vice versâ*. In order to distinguish these two opposite powers from each other, that power which is obtained from the glass has been termed *vitreous* or *positive* electricity: that from the wax *resinous* or *negative* electricity.

Let us suppose that the paper disk has been charged by means of the glass tube, so that it is repelled on attempting to bring the glass near it; this state will be retained by the disk for many minutes. This contrivance forms, in fact, an *electroscope*, for it furnishes a means of ascertaining whether a body be electrified or not, and even of indicating the kind of electricity. Suppose that a body suspected to be electrified is brought near the disk, which is in a state repulsive of the glass tube; if repulsion occur between the disk and the body which is being tested for electricity, it is at once obvious that the substance is electrified; and moreover, that it is vitreously electrified, since it produces an effect similar to that which would be exhibited by an excited glass tube.

The phenomena of attraction and repulsion may be further exemplified by the following experiments:—Suspend two straws, separately, by a fibre of silk, each to a glass rod (fig. 169); bring an excited stick of sealing-wax towards each; each will be first attracted and then repelled; whilst thus repulsive to the wax, bring the one near to the other; they will recede from each other as they did from the wax. If both straws be excited by glass, they will in like manner repel each other; but if one be excited by the glass and the other by the wax, they will attract each other. Hence we learn, that bodies similarly electrified repel, those differently electrified attract each other.

Fig. 169.



Proceeding a step further, it will be found that whenever two bodies are rubbed together, both kinds of electricity are liberated,

but so long as the two bodies remain in contact, no sign of the presence of either electricity appears; on separating them, both are found to be electrified—one vitreously, the other resinously; for example, stretch a piece of dry silk over a brass plate, and rub it upon a glass plate; so long as the two bodies are in contact, the quantities of each kind of electricity set free are precisely sufficient to neutralize each other, and the combined plates will not affect the electroscope, but as soon as the glass plate and the silk are separated, the glass will repel the disk (fig. 168), while the silk will attract it.

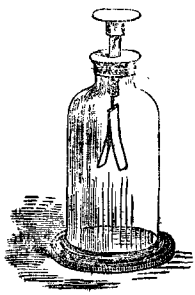
(225) *Insulators and Conductors.*—Bodies that have been thus electrically excited, return to their neutral condition when touched by other substances, but with degrees of rapidity depending on the kind of body which touches them. A rod of sealing-wax or of shell-lac, for example, may be held in contact with any electrified body without sensibly lessening the charge; but the momentary touch of a metallic wire, or of the hand, is sufficient to remove all indications of electric excitement: it is therefore clear that there are some bodies which, like the wire or the hand, readily allow the passage of electricity, and these are termed *conductors;* whilst there are others which, like shell-lac, do not easily allow its passage, and these are called *insulators.* There is, however, no absolute line of distinction between these two classes of bodies; there is no such thing as either perfect insulation, or perfect conduction, for the two classes of bodies pass gradually one into the other.

In the following table each substance enumerated is superior in insulating power to all those which follow it. The nearer the substance is to the bottom of the table, the better, on the contrary, is its conductivity:—

Insulators.	
Dry Gases and Dry Steam.	Spermaceti.
Shell-Lac.	Turpentin and Volatile Oils.
Sulphur.	Fixed Oils.
Amber.	String and Vegetable Fibres.
Resins.	Moist Animal Substances.
Caoutchouc.	Water.
Gutta Percha.	Saline Solutions.
Diamond, and some other precious stones.	Flame.
Silk	Melted Salts.
Dry Fur..	Plumbago.
Glass.	Charcoal.
Ice.	All the Metals.
	Conductors.

Any object is spoken of as being electrically *insulated* when it is supported by means of some badly-conducting substance which prevents the free escape of the electricity. The presence of moisture deposited from the air upon the surface even of the best insulator converts it for the time into a conductor, and is one of the most annoying impediments to the success of electrical experiments, as the electricity is carried off as fast as it is accumulated. Glass is especially liable to this inconvenience, but by varnishing it when practicable, and keeping it thoroughly warm, the difficulty is diminished. By due precautions, instruments may be constructed which, in dry air, will preserve a charge for a considerable time, weeks or months.

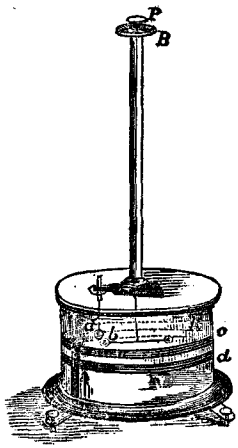
FIG. 170.



The most perfect insulators still allow electric attraction to traverse them, although by a process different from conduction, and hence they are termed *Dielectrics* (230). For instance, if one side of a plate of glass be electrified by rubbing it with a piece of silk, the opposite face also acquires the power of attracting particles of bran or other light objects.

(226) *Electroscopes.*—Various instruments have been devised for detecting feeble charges of electricity. One of the most convenient of these is the *gold-leaf electroscope* (fig. 170), which is sensible to extremely small charges. It consists of a pair of gold leaves suspended from the lower extremity of a metallic wire which terminates above in a brass plate. The wire is insulated by passing it through a varnished glass tube packed with silk, and the whole is surrounded and supported by a glass case. The approach of an excited body instantly causes the divergence of the leaves. If a glass tube be rubbed with a dry handkerchief, and touched with a small disk of paper insulated by attaching it to a rod of sealing-wax, as directed in preparing the electroscope (fig. 168), a small vitreous charge will be received by the paper, and if carried by it to the cap of the electroscope, the leaves will diverge permanently with vitreous electricity. The approach of the glass rod would cause the leaves to diverge further, whilst that of a stick of excited wax would cause them to collapse.

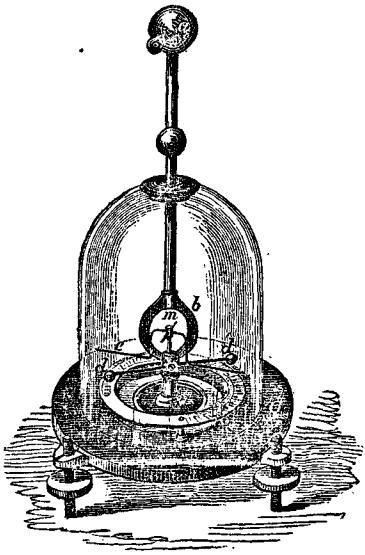
FIG. 171.



An instrument (fig. 171) called a *torsion electrometer* was devised by Coulomb for accurately measuring minute differences in the amount of electrical attraction or repulsion. The force which he opposed to that of electricity was the resistance to twisting which is offered by an elastic thread. A fibre of silk, a fine silver wire, or a thread of glass, has been used for the purpose of measuring the angle of torsion, this angle being exactly proportional to the force applied for small displacements.

By means of a long glass thread, fastened above to a pin, P (carrying an index which traverses the graduated plate, B), a needle of shell-lac is suspended freely in the glass case, A. This needle is terminated at one end by a gilt ball, *b*, at the other by a paper disk which serves to check its oscillations. In the glass cover of the instrument is a small aperture through which another gilt ball, *a* (the *carrier*), also suspended by shell-lac, can be introduced and withdrawn. In order to equalize the induction, two narrow strips of tinfoil, *c* and *d*, connected with the earth, and having a narrow interval between them, are pasted upon the inside of the glass cylinder, one a little above and the other a little below the level of the balls; a graduated circle is pasted on the glass for reading off the angular deviation of the needle. When the instrument is to be used, the carrier-ball is adjusted so that after it has been removed it can with certainty be replaced in the same position as at first; the ball upon the needle is adjusted by turning the pin until, without any twist upon the thread, it shall just touch the carrier, its centre being at the zero of the scale, and the position of the index on the upper graduated plate, B, is noted. The carrier-ball, *a*, is next made to touch the object the electricity of which is to be measured: it takes off a quantity proportional to the amount accumulated on the spot. The ball *a* is immediately replaced in the instrument; it divides its charge with the ball *b* on the needle, and repulsion ensues. The thread which supports the needle is then twisted until the centre of the ball *b* is, by the reaction of torsion, brought back towards the carrier, *a*, to some determinate angle (say 30°) marked on the graduation of the glass case; suppose the number of degrees through which it has been necessary to twist the thread to be 160°; 160 + 30, or 190, will represent the repulsion. To compare this amount with any other quantity, the balls must be discharged, and the experiment repeated under the new conditions, noting the number of degrees of torsion required to make the needle stand at 30° as before: the repulsion is directly proportional to the torsion angle in the two cases. Suppose in a second experiment that the thread sustain a twist of 180° before the ball *b* is brought back to the angle of 30°; the repulsion will now be 180 + 30, or 210; and the relative electrical repulsions in the two experiments will be as 190 : 210.

FIG. 172.



Another very convenient electrometer was devised by Peltier, in which the directive force exerted by the earth upon a small magnet is substituted for the torsion of a wire. Fig. 172 represents Peltier's electroscope: *a b* is a metallic wire terminating above in a brass knob, and cemented by means of shell-lac into an insulating foot of ebonite, C. At *b* is a brass ring, from which proceed two brass arms, *d d*. In the ring is supported a light metallic needle, *e*, which moves freely upon a pin like a compass-needle. This metallic needle carries a small magnetized steel wire, *m*. In order to use the instrument, it is placed so that the needle, *e*, when the steel wire, *m*, is exactly in the magnetic meridian, is just made to touch the arms, *d d*. On communicating a charge of electricity to the

ball, *a*, it spreads over the insulated wire and needle, *e*; the needle is immediately repelled by the fixed arms, *d d*, and the amount of its angular deviation gives the means of estimating the repulsion; this, however, is not directly proportionate to the number of degrees which represent the angle of deviation. These values must be ascertained by direct experiment.

The most perfect form of instrument yet produced is Sir William Thomson's *quadrant electrometer.* (*Report of Committee on Standards of Electrical Resistance. British Association Report for* 1867, 490.) The needle consists of a thin aluminium plate, narrower in the centre than at the ends, and with the ends rounded off; through the centre of the plate a platinum wire is fixed, with a short cross-piece at its upper end, to which are attached two fibres of unspun silk, by which the wire and needle are suspended. The needle is placed within a flat circular box of brass, divided into four quarters, and with the centre cut away to permit the passage of the suspending wire and its prolongation. These quadrants are attached by insulating glass stems to the brass cover of a Leyden jar containing concentrated sulphuric acid as the inner coating, and coated externally with tinfoil. To the platinum wire below the needle is attached a piece of finer wire supporting a platinum weight, which hangs in the sulphuric acid, and the needle is thus kept charged with electricity when the apparatus is in use; a small concave mirror is fixed to the platinum wire above the needle, and by its means very small movements of the needle are rendered visible by the motion of the image of an illuminated slit or wire on a screen placed at some distance from the mirror. The quadrants are so mounted that their edges are not in contact, but the opposite quadrants are connected by metallic wires; two binding-screws are fixed to the lid of the instrument, by which a charge may be communicated to the quadrants. The silk fibres are placed in such a position that when the quadrants are discharged the needle stands over the spaces between the pairs of quadrants, and they bring the needle back into this position if displaced from it. In order to use the instrument, the Leyden jar is charged with positive electricity. It is essential that this charge should be constant, and the force of the charge is measured by the attraction experienced by a light aluminium plate placed at the top of the instrument, opposite a brass plate in connexion with the interior coating of the jar; the charge of the jar is increased or diminished by means of the replenisher, which raises the charge when a milled head is turned in one direction, and lowers it when turned in the other, but for a description of which the reader must be referred to the original paper. If now a feeble charge be communicated to one pair of the quadrants while the other pair is connected with the earth, or charged equally and oppositely, the needle will be attracted by one pair and repelled by the other, and will consequently rotate on its axis in a direction determined by the arrangement of the connexions of the quadrants. This instrument is so delicate that a single cell of Daniell will cause the spot of light on the scale to move over 60 divisions (of $\frac{1}{40}$ of an inch at a distance of 40 inches)—a very considerable effect if we consider the very low tension of the electricity at the poles of a voltaic couple (259).

It was long imagined that non-conductors only were capable of excitement by friction, and hence they were termed *electrics;* all bodies, however, exhibit this phenomenon, if proper care be taken to insulate them. If, for example, a piece of brass tube insulated by a glass handle be rubbed upon fur, it receives a charge, as may be shown by bringing it near the disk of the electroscope (fig. 168). Even two dissimilar metals, after being brought into contact with each other, may, with proper precautions, be made to

show signs of electric excitement on being separated (257). The friction of glass against metal spread over silk is attended by a more powerful development of electricity than when silk alone is used; and an *amalgam* consisting of 1 part of tin, 2 of zinc, and 6 of mercury, rubbed to fine powder and mixed with a little lard, is found to be highly effectual in exalting the quantity which is developed. The same substance, however, does not always manifest the same electrical condition when rubbed; glass when rubbed upon silk becomes vitreously excited; but if rubbed on the fur of a cat it exhibits resinous electricity. Metallic bodies, when their surface is perfectly free from oxide, become negatively electric when rubbed by imperfect conductors such as silk, fur, wood, cork, or ivory. The amount of friction necessary to produce electric excitement is exceedingly small; the mere drawing of a handkerchief across the top of the electroscope (fig. 170), or even across the clothes of a person insulated by standing on a cake of resin, or on a stool with glass legs, provided he touch the cap of the instrument, is sufficient to cause divergence of the leaves. The simple act of drawing off silk stockings, or a flannel waistcoat, or the combing of the hair in frosty weather, frequently occasions the snapping and crackling noise due to the electric spark; and the stroking of the fur of a cat at such a season is well known to produce similar effects.

(227) *Electrical Hypotheses.*—These various phenomena have been accounted for by two principal hypotheses.

One of these, commonly known as the 'theory of one fluid,' is due to Franklin. Electricity, upon this view, is supposed to be a subtle imponderable fluid, of which all bodies possess a definite share in their natural or unexcited state. By friction or otherwise, this normal state is disturbed. If the body rubbed receive more than its due share, it acquires vitreous electricity, or, in the terms of Franklin, becomes electrified positively, or + ; whilst at the same time the quantity of electricity in the rubber which becomes resinously charged is supposed to be diminished, and thus the rubber acquires a negative or — state. Franklin supposed the particles of the electric fluid to be highly self-repulsive, and to be powerfully attractive of the particles of matter.

The other hypothesis, the 'theory of two fluids,' was originally proposed by Dufay. According to this view there are two electric fluids, the vitreous and the resinous, equal in amount but opposite in tendency; when associated together in equal quantity they neutralize each other perfectly; a portion of this compound fluid pervades all substances in their unexcited state. By friction the

compound fluid is decomposed; the rubber acquires an excess of one fluid, say the resinous, and thus becomes resinously excited; the body rubbed takes up the corresponding excess of vitreous electricity, and becomes excited vitreously to an equal extent. Upon this view the particles of each fluid are self-repulsive, but powerfully attract those of the opposite kind.

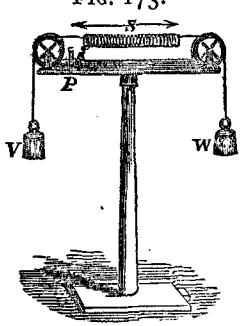
The language of either theory may be employed in order to distinguish the two kinds of electricity: the term vitreous or positive may be used indifferently for one kind, and resinous or negative for the other kind, provided it be borne in mind that positive and negative are mere distinguishing terms: negative electricity being as real a manifestation as the positive.

It is manifest that one or other of these hypotheses must be false, yet either will serve to connect the facts together. The supposition of an electric fluid is, notwithstanding, gradually being abandoned. The supposition of a gravitative fluid might, with nearly as much propriety, be insisted on to explain the phenomena of gravitation, or a cohesive fluid to account for those of cohesion.

Electricity is now regarded as a stress in a medium, remarkable for the peculiar form of action and reaction which it exhibits. This kind of action and reaction follows the same law of equality and opposition in its manifestations as that which is exhibited more obviously in the phenomena of mechanics. Whenever vitreous electricity is manifested at one point, a corresponding amount of resinous electricity is invariably developed in its vicinity, reacting against it, and thus enabling its presence to be recognised, although this reaction may not be immediately perceptible.

The phenomena of vitreous and resinous electricity may be rudely but not inaptly illustrated by those of elasticity exhibited by an ordinary spring, as shown at s, fig. 173. The spring in its unstretched state may represent the body in its unelectrified condition; it then displays nothing of the peculiar power that it possesses. The spring cannot be stretched from one extremity only; but if fixed at one end, as by hooking it to the pin, P, a weight, W, may be applied to the other end, and it will seem to be stretched by one weight only. In reality, however, it is not so; for by substituting at V a weight equal in amount to that at W, instead of the fixed point, P, the tension of the spring remains

Fig. 173.



unaltered, but a reaction, equal and opposite to the original action of the weight, w, is instantly rendered evident.

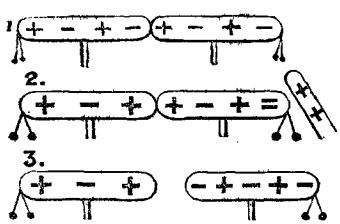
So it is with electricity; cases not unfrequently occur where one kind only of electricity seems to be present, but a careful examination will always detect an equal amount of the opposite kind. This essential character of action and reaction in the electrical force will be more clearly manifested in the following remarks and experiments.

(228) *Electrical Induction.*—In the preceding cases the electricity has been excited by friction and communicated to other bodies by contact. An insulated charged body, however, exerts a remarkable action upon other bodies in its neighbourhood. Long before contact occurs, the mere approach of an excited glass tube towards the electroscope causes divergence of the leaves, and on removing the glass tube, if it have not been allowed to touch the cap of the instrument, all signs of disturbance cease.

The following mode of performing the experiment will afford a means of examining this action of an electrified substance upon objects at a distance:—

Place two cylinders of wood, or of metal, each supported on a varnished stem of glass, so as to touch each other end to end (fig. 174, 1); from the outer extremity of each suspend a couple of pith balls by a cotton thread, and bring the excited glass tube near one end of the arrangement as shown at 2. Electric disturbance will be shown by the repulsion of both pairs of balls. Separate the two cylinders without touching the conducting portion, and then remove the glass tube; the balls will still continue to diverge (3). But let the glass be again brought near; the balls on the cylinder originally *nearest* the glass will collapse, showing this cylinder to be *negatively* excited, while the same excited glass will cause the balls on the *further* cylinder to diverge from the presence of *positive* electricity. Again, remove the glass altogether, and bring the two cylinders into contact; a spark may generally be seen to pass between them, and both pairs of balls will immediately collapse and continue at rest. The entire amount of electricity existing upon the two cylinders taken together remains the same throughout the whole period of the experiment, but its distribution

Fig. 174.

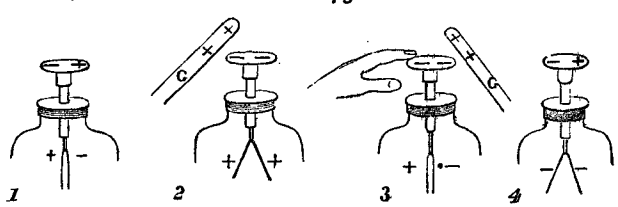


is altered, as is shown by the position of the signs + and −. The experiment may be explained in the following manner:—Suppose the two cylinders to be in the neutral state (No. 1); on bringing the excited glass tube near to them, a portion of the negative electricity appears to be drawn towards the end of the cylinder nearest to the glass, as in No. 2, whilst the corresponding quantity of disengaged positive electricity causes the balls on both cylinders to diverge: the moment the glass is removed, the negative electricity redistributes itself as in No. 1, and the balls collapse; but if the two cylinders be separated before the glass is removed, and if the excited glass be then withdrawn,* the results will be such as are represented in No. 3, in which the negative electricity on one of the cylinders is more than sufficient to neutralize the positive, and hence the balls diverge negatively; while on the other it is less than sufficient for the positive, consequently the balls diverge with positive electricity. On causing the two cylinders to approach each other when in this state, the two electricities will neutralize each other, and if of sufficient power, the reunion will be attended with a slight spark.

This action at a distance of one electrified body upon others in its neighbourhood is termed *electrical induction*. It is a principle of very extensive application, and indeed it furnishes a key to the explanation of the greater number of electrical phenomena.

An instance of electrical induction is afforded in the action of the gold-leaf electroscope. Let 1 (fig. 175) represent the instru-

FIG. 175.



ment in a neutral state. As soon as an excited glass tube, G, is caused to approach the cap of the electroscope, the leaves will

* If the glass tube be withdrawn *gradually* to a certain distance, the balls upon the cylinder nearest the tube will gradually collapse, in proportion as the inductive power is weakened by distance; a portion of the negative electricity being liberated in quantity sufficient to neutralize the free positive charge, and, on completely withdrawing the excited tube, the excess of negative electricity is set free, and the balls now diverge negatively.

diverge as at 2. Whilst the glass tube is still near the instrument, let the cap of the electroscope be touched with the hand, so as to uninsulate it for a moment, as at 3, by placing it in communication with the earth through the body, which acts the part of a conductor; the leaves will collapse, and the instrument will seem to be quiescent; now remove the finger from the cap, and then take away the glass tube, G; instantly the leaves diverge, and the electroscope is permanently charged, in consequence of a change in the distribution of the electricity, as represented at 4. Its charge, however, is not positive like that of the glass, but negative; for if the glass be again brought near, the leaves will collapse, while a stick of excited wax will make them open out further. These effects arise from electrical induction. and the process which takes place is believed to be the following. The approach of the tube in the first instance causes the negative electricity to accumulate in the cap, as at 2, where it is retained by a species of attraction, in which condition it is said to be *disguised*. The leaves, therefore, diverge with a corresponding quantity of positive electricity thus set free; things being in this state, a touch is sufficient to neutralize the excess of positive electricity, as seen in 3, and the instrument appears to be quiescent. Remove first the finger, and then the glass tube, however, and the negative electricity, that had been accumulated on the surface of the cap, spreads over the whole instrument (though in the diagram this is only represented as taking place upon the leaves), and the leaves diverge with negative electricity, as shown at 4.

In all these cases, the excited body itself neither loses nor gains electricity by the process just described. The mode in which this transfer of force from a distance is effected still remains to be considered.

(229) *Faraday's Theory of Induction.*—We owe to Faraday a theory of these effects, which has been thus concisely summed up by Snow Harris (*Rudimentary Electricity*, second ed., pp. 44, 45, 47). Faraday 'conceives electrical induction to depend on a peculiar form of physical action propagated between contiguous molecules. In these intermediate molecules, a separation of the opposite electricities takes place, and they become disposed in an alternate series or succession of positive or negative points or poles; this he terms a *polarization* of the particles, and in this way the force is transferred to a distance. Thus, if in fig. 176, P represent a positively charged body, and *a, b, c, d,* interme-

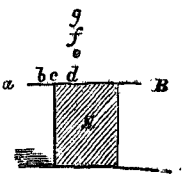
diate molecules, then the action of P is transferred to a distant body, N, by the separation and electrical polarization of these particles, indicated by the series of black and white hemispheres. Now, if the particles can maintain this state, then insulation obtains; but if the forces communicate or discharge one into the other, then we have an equalization or combination of the respective and opposite electricities throughout the whole series, including P and N.' . . . . 'This theory . . . . considers particles of common matter, taken as centres of force, as being more or less conducting; the particles not being, in their quiescent state, arranged in a polarized form, they become so by the influence of contiguous and charged particles. They then assume a forced state, and tend to return, by a powerful tension, to their original normal position; being *more* or *less* conductors, the particles charge either *bodily* or by *polarity;* contiguous particles can communicate their forces more or less readily one to the other. When less readily, the polarized state rises higher, and *insulation* is the result: when more readily, *conduction* is the consequence.' . . . . 'Induction is the action of a charged body upon insulating matter, or matter the particles of which communicate the electrical forces to each other in an extremely minute degree.'

FIG. 176.

(230) *Distribution of Electric Charge.*—Bodies susceptible of this polarization are termed *dielectrics;* and whether they be solid, liquid, or aëriform, the electric action is transmitted through them freely. A pane of glass interposed between the excited tube and the cap of the electroscope will in no sensible manner affect the divergence of the leaves, which will occur as usual; but the interposition of an uninsulated sheet of tin-plate, or even of a screen of wire gauze, will effectually stop all signs of electric excitement on the leaves.

Owing, however, to the molecular action by which induction is propagated, Faraday has shown that it may, under certain circumstances, be traced round the edges of such a screen, and it may be continued either in *curved* or in straight lines. Let s (fig. 177) represent a mass of shell-lac which has been excited by friction at its upper part; B, a brass-plate resting on the shell-lac, but also in conducting communication with the ground. At *a*, a strong inductive action is perceived, which

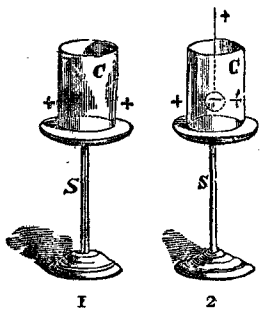
FIG. 177.



is weaker at *b*, weaker still at *c*, and very trifling at *d*; at *e* it increases, and at *f* is nearly as strong as at *b*, whilst at *g* it again decreases, from the effect of increasing distance.

In consequence of these inductive actions, electricity when at rest is always distributed over the surface of a charged object; and therefore, for the purpose of collecting electricity, a hollow shell of conducting matter is quite as effectual as a solid mass of the same size. Many striking experiments may be given in proof of this important fact. For instance, place a metallic can, c (fig. 178, 1), upon a small insulating stand, s; communicate a charge to a brass ball, insulated by a slender glass rod, and introduce this charged ball into the interior of the can, allowing it to touch the bottom; withdraw the ball; it will be found when tested with the electroscope to have given up all its electricity. Touch the inside of the can with a *proof plane* (or small disk of paper insulated by a stout filament of shell-lac) and hold it towards the charged disk of the electroscope (fig. 168), no action will be perceived: bring the proof plane, however, into contact with any part of the outer surface of the metallic can, and an abundant charge will be obtained. No charge can be sustained towards the interior, because there is no object within towards which induction can take place; but the polarization of the air on the outside produces induction towards all surrounding objects.* But now, whilst the exterior still remains charged, hold an unexcited brass ball, attached to a metallic wire, in the inside of the cup (fig. 178, 2), without, however, allowing it to touch it; if the insulated paper disk, under these circumstances, be made to touch any part of the inside of the can, it will receive a charge: the particles of the air within the can may, under these circumstances, become polarized, because the brass ball is in a condition to become oppositely charged to the can. If the can be positive, the ball becomes negative, its positive electricity passing off to the earth by the wire.

FIG. 178.



On this principle Sir W. Thomson has constructed a self-acting apparatus for multiplying and maintaining electric charges (*Proc. Roy. Soc.* 1867, xvi. 67). A vertical cylinder of copper, open at both ends, is connected to the stem of a Leyden jar: in the centre of the cylinder is the end of an uninsulated tube delivering water in drops. The jar is charged, say, positively, and the cylinder then acts by induction on the water at the end of the tube, and as the drops break away they carry with them a negative charge. At a short distance below the cylinder another is fixed, connected with the interior coating of a second Leyden jar. This cylinder has within it a copper funnel, on which the drops fall, and so charge the jar negatively. The water falls through this funnel, but without carrying away any of the charge. The second Leyden jar is also connected with a copper cylinder or inductor, in which a second uninsulated stream of water is breaking into drops; but as this jar is negatively electrified, the drops are acted upon inductively, and carry away a positive charge, which is collected by a receiver similar to the first, but connected with the first Leyden

* Indeed, a delicate electrometer may be enclosed in a shell of conducting matter, which may be so highly charged as to emit sparks in all directions, though the electrometer will remain wholly unaffected.

jar. In this way a rapid succession of sparks may be obtained, though the charge given to the first Leyden jar was extremely small.

A similar disturbance of electric equilibrium will be found whenever a charged body is brought near other uninsulated ones. If an excited glass tube be brought towards the wall of the room, and just opposite to the tube the wall be touched with the proof plane, a small charge of resinous electricity will be carried off, and will be perceptible by the electroscope.

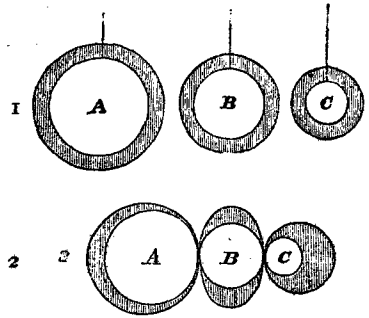
By increasing the surface of the conductor whilst the amount of electricity remains the same, it is obvious that the quantity upon each portion of exposed surface is diminished, and the *tension* of the charge is said to be lowered. For instance, if a metallic ribbon, coiled up by the action of a spring, be attached to the cap of an electroscope, and a small charge be given to it, a certain divergence of the leaves will be produced: on uncoiling the ribbon, by means of a silk thread attached to it for the purpose, the leaves will partially collapse, because the same amount of induction towards the ceiling and floor of the room is now distributed over a larger surface; but on allowing the spring to exert its elasticity and coil up the ribbon, the leaves will again resume their original divergence.

In all cases of electric excitement the charge is diffused over the surface of the conductor, but the form of that surface materially influences the mode in which the electricity is distributed. If a charged sphere be suspended in the centre of a room, the superficial distribution of the electricity will be uniform on all parts of its surface. But if two similar and equally excited spheres be suspended side by side, the electric accumulation will be greatest at those points of their respective surfaces which lie at the opposite extremities of a line passing through the centre of each; and, in a charged cylinder, the electrical density is greatest at the two ends.

This change in the distribution of electricity over the surface, which depends upon the change of form, was carefully investigated by Coulomb. For this purpose he employed his torsion balance, shown at fig. 171. The carrier-ball, *a*, of the instrument was brought into contact with that point of the conductor which was to be examined; the ball thus acquired a charge proportional to the density of the electricity at that spot; and the tension was measured in the manner already described (226), by the angular repulsion of the needle; different points of the conductor were thus examined in succession, and the tension at each point was compared with the others.

In this way it was found that if two spheres of unequal diameters were each originally electrified to the same degree of density (that is, if each sphere were so charged that the quantity of electricity upon a square inch of the surface of each was exactly equal, when the two were separate) on bringing the two into contact, the greatest accumulation still occurred at the extremities of a line joining the centre of the spheres, but the accumulation was greater on the small ball than on the large one. The experiment may be carried still further: for if a series of spheres gradually diminishing in size be employed, till at last they virtually end in a point, the accumulation at length becomes so great that the point is unable to retain the charge, and dispersion ensues.

FIG. 179.

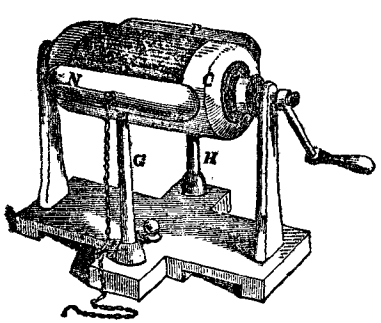


A rough idea of this effect may be conveyed by fig. 179, in which A, B, and C represent three independent spheres diminishing in size, and which in No. 1 are supposed to be charged with electricity of uniform density, as represented by a shaded layer of equal thickness around each, while No. 2 represents the same three balls in contact. The superficial density of the charge, as shown by the lines of shadow, is proportionately much greater on the smallest ball than on the largest. Points must therefore be carefully avoided in the construction of apparatus for retaining electricity. For similar reasons sharp or rough edges are equally objectionable.

(231) *Electrical Machines.*—In order to obtain large supplies of electricity, the electrical machine is employed. Two principal forms of this instrument—viz., the *cylinder* and the *plate* machine, are in general use.

In the cylinder machine (fig. 180) a hollow cylinder of glass, C, is mounted on a horizontal axis turning by a winch in two strong wooden supports. On one side is placed a leather cushion, R, stuffed with hair and faced with silk; from its upper edge proceeds a silk flap, S, which reaches nearly round the upper half of the cylinder. N is a brass conductor for collecting electricity from the rubber. The cushion is insulated

FIG. 180.

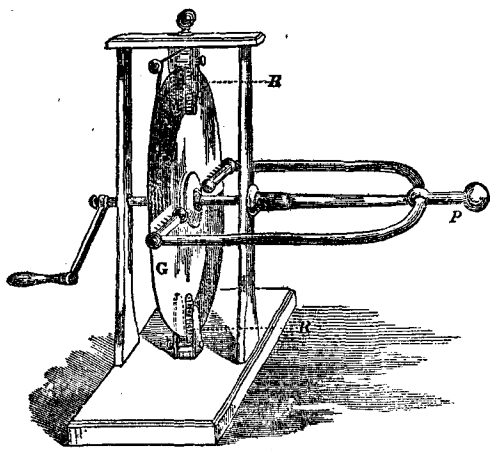


by a strong glass pillar, G. To collect the electricity from the glass a metallic conductor, P, is mounted on an insulating stem of glass, H; this conductor, on the side next the glass, is furnished with a row of points, which, from the high electrification and consequent disruptive discharge produced upon them, act as powerfully in receiving as in dispersing a charge. Before using the machine, a little of the amalgam of zinc and tin (226) is spread over the surface of the cushion. When the whole is made properly dry and warm, on turning the handle a brisk, cracking, snapping noise is heard, whilst flashes and sparks of fire dart round the cylinder from the edge of the silk flap. Sparks of two or three inches (5 or 6 centimetres) in length may now be drawn from the *prime conductor*, P, if the hand be applied to the rubber when the cylinder is turned. In order to obtain a continuous supply of sparks from the conductor, P, it is, however, absolutely necessary to maintain a conducting communication between the rubber and the ground. If the prime conductor be made to communicate with the ground while the rubber is insulated, sparks may be freely obtained from the rubber on working the machine. The electricity from the cylinder and conductor, P, however, is positive, like that from glass generally, whilst that from the rubber is negative. If the rubber and the conductor, while both are insulated, be connected by a metallic wire, no sparks can be obtained from either, however vigorously the machine be worked, the negative electricity of the rubber being exactly neutralized by an equal amount of positive electricity from the cylinder and conductor. The reason why it becomes necessary, in working the machine effectively, to connect either the rubber or the conductor, P, with the earth, is thus rendered obvious, since otherwise induction takes place between the liberated resinous electricity on the rubber and the positive electricity which accumulates on the prime conductor, and thus prevents its free discharge. No sooner, however, is the negative electricity in the rubber supplied from the unlimited stores of the earth with an equivalent amount of positive electricity, through a chain suspended to it, or through the body by placing the hand on the rubber, than the accumulated positive electricity on the conductor, P, is free to pass off in sparks to such objects as are sufficiently near.

In the *Plate Machine* (fig. 181), a flat plate of glass, G, is substituted for the cylinder, C, in fig. 180. The axis of rotation passes through the centre of this plate, and the rubbers, R, R, are placed on each side of the glass along a portion of its circumference. In this form, however, it is not easy to insulate the

rubbers, and to obtain negative electricity separately, though it supplies positive electricity in abundance. P is the prime conductor, insulated by a glass stem.

FIG. 181.



Instead of glass plates, ebonite ones are now frequently used for electric machines, they give very powerful sparks, and are less fragile than glass. The electricity is, of course, negative, but this matters little in the ordinary use of the machine. When, however, the rubber is covered with amalgam, the electricity is positive.

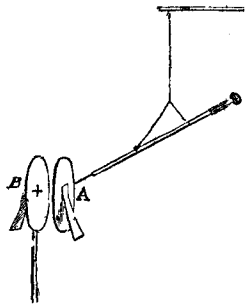
The action of the electric machine may also be explained by the principles of induction. The glass plate, by friction with the amalgam, becomes charged positively and acts by induction on the natural electricity of the prime conductor, repelling the positive fluid and attracting the negative to the points, where it is discharged on to the plate neutralizing the positive electricity of the latter. When a conductor in communication with the ground is brought near the prime conductor, its positive electricity is repelled to the earth and the negative attracted, and a discharge may take place when the positive fluid of the prime conductor is neutralized by the negative fluid attracted from the earth. The plate after passing the points has its electricity in the natural state, but when brought in contact with the rubber the positive fluid remains on the plate, the negative passing through the rubber to the earth.

(232) *Extensive Operation of Induction.*—As the principle of induction already explained is one which pervades the whole phenomena of electricity, we proceed to point out a few more examples.

Every case of attraction is preceded by induction: the opposed surfaces become oppositely electrified by polar action, after which attraction ensues. The following elegant experiment by Snow Harris shows the steps of the process clearly:—Attach to a circular disk of gilt card, A, fig. 182, about three inches, or seven centimetres, in diameter, one end of a slip of gold leaf, and by a rod of shell-lac fasten the disk to a light strip of wood, balanced at the other

end by a weight. Suspend this freely by a thread, as represented in fig. 182; on bringing another similarly insulated charged gilt disk, B, near A, the gold-leaf upon A will diverge, and then attraction of the disk will follow.

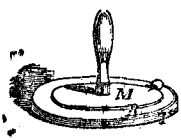
FIG. 182.



The phenomena of electrical repulsion also may be traced to induction. If a pair of slips of gilt paper be insulated and suspended side by side as in the electroscope, they will diverge when charged; whilst in this condition a proof plane will detect no electricity on their inner surfaces, but abundance on the outer ones: induction takes place towards surrounding objects, which attract the leaves, and they separate from each other: but if any conducting body in communication with the earth be introduced between the two leaves, induction now takes place from the inner surface of the leaves towards it, and they instantly collapse. Many amusing electrical experiments have been contrived upon the principle of induction: light figures, placed on a conducting surface under an electrified plate, are made to dance by alternate attractions and repulsions. If a number of strips of paper be supported in the centre of a room, by attaching them to a wire which is in connexion with the conductor of a powerful machine in action, they will rise up and diverge in all directions, towards the ceiling, the walls, and the floor, under the influence of induction; if a conducting point or surface be brought near them, they will all bend over and converge towards it.

(233) *Electrophorus.*—The electrophorus of Volta is an inexpensive and portable kind of electrical machine which derives its name from ἤλεκτρον, and φορὸς carrier, in allusion to the manner in which the metallic cover carries electricity: it owes its activity to the operation of induction, which indeed it is well calculated to exemplify. The instrument (fig. 183) consists of a resinous plate R, 12 or 15 inches (30 or 40 centimetres) in diameter, which may be composed of equal parts of shell-lac, resin, and Venice turpentin, melted together and cast into a circular cake of about an inch (25 millimetres) in thickness. This cake rests on a sheet of tin-plate or metal, T; it is furnished with a moveable cover consisting of a somewhat smaller circular metallic plate M, to which is attached an insulating handle. The resinous cake is rubbed with warm and dry fur or flannel, and on then putting down the metallic cover by its insulating handle, a spark of negative electricity may be drawn from it; on again raising it, a spark still brighter, of positive electricity, may be obtained. On replacing the cover, another negative spark may be drawn, and on raising it, another positive one, and these alternate effects may be obtained for an indefinite number of times.

FIG. 183.



The action of the electrophorus may be thus explained. When

the cake is rubbed, it becomes negatively electrified on its upper surface, the under surface, which is in communication with the earth through the tin-plate, becomes by induction, positive to a similar extent, the particles of the cake being thrown into a polar condition. It thus polarizes the metallic plate on which it rests, liberating negative electricity, and this passes off to the earth, whilst the metal preserves a positive charge, which, being retained by induction, is not perceived until the inductive action of the upper surface is directed to the metallic cover. If the metallic cover be now brought down upon the upper surface of the cake, it touches the resin on a few points only, and from the inferior conductivity of the resin receives but little direct negative charge from the contact; instead of this, the under surface of the metal becomes positive by induction from the resin, whilst upon its upper surface a corresponding amount of negative electricity is set free: this escapes in the form of a spark, if a conductor be presented. On raising the cover after the escape of the negative spark, the positive electricity, which before was attracted to the lower surface of the metallic cover and held there by induction, is in excess, and it is ready to escape as a spark when a conductor is presented near enough to it. As the resin has lost none of its charge, the process may be repeated for an indefinite number of times.* If after the resinous cake of the electrophorus has been excited in the usual manner, it be placed upon an insulating support, and the metallic cover be brought down upon it by means of the insulating handle, little or no negative electricity will be obtained from the upper plate on connecting it with the ground: but if a connexion be made between the upper and under metallic plate by touching one with each hand, a slight shock will be felt (235) owing to the neutralization of the positive electricity of the lower plate by the liberated negative of the upper. On now raising the cover, a positive spark may be obtained, and on replacing the discharged cover upon the resin, the same series of phenomena may be repeated as often as the operator pleases without exciting the resin anew.

(233*a*) *Holtz's Machine.*—M. Holtz of Berlin (*Pogg. Ann.*, 1865, cxxvi. 157) has invented an electric machine which is a

* The correctness of this explanation may be verified by substituting for the metallic cover a circular disk of tinfoil of the same diameter, and pressing it down into complete contact with the resinous plate; on removing the tinfoil it will be found to have discharged the resinous plate completely; and no charge will now be communicable to the insulated metallic cover until the surface of the resin has been excited afresh by friction.

kind of revolving electrophorus. It consists of a circular glass plate well varnished which can be caused to rotate with great rapidity. About $3^{mm.}$ from this is a fixed varnished glass plate of a diameter about 2 inches greater than the moveable one. The fixed plate has two apertures or windows cut in it at the opposite ends of its horizontal diameter, and, on the upper side of one window and on the lower side of the other, armatures of paper with tongues of card projecting to the centre of the window are attached. Opposite the armatures, but on the other side of the rotating plate, are conductors provided with combs: to these conductors sliding rods and balls are attached, so that the latter may be brought into contact when necessary. In order to set the machine in action the balls of the conductors are brought together and the plate set in motion, one of the paper armatures is then electrified positively by bringing near to it a piece of excited ebonite which is negatively electrified, this acting by induction on the natural electricity of the armature repels the negative fluid which is discharged by the tongue on to the revolving plate, the positive electricity remaining on the armature. The armature now acts by induction on the electricity of the conductor drawing the negative fluid from the comb on to the revolving plate and repelling the positive. The plate, now negatively charged at this place, makes a half revolution and communicates a negative charge to the other armature, which, acting by induction on the electricity of the other conductor, attracts the positive fluid through the comb on the glass plate, the negative being repelled along the conductor. The two conductors thus become oppositely charged, and on separating the knobs long sparks pass between them.

It will be seen that while the plates are revolving the paper armatures are kept charged, and, under favourable conditions, the charge will be retained for some time. If, however, the machine is enclosed in a case in which the air is kept dry by means of pumice stone moistened with sulphuric acid, it will remain charged for 24 hours. The case has besides the great advantage of excluding particles of dust, which, when attracted by the electrified plates, interfere seriously with the efficiency of the machine.

(234) *Spread of Induction.*—A remarkable peculiarity in electrical induction has yet to be noticed. When a charged sphere, A, is suspended exactly in the centre of a hollow uninsulated spherical conducting envelope, B, fig. 184, induction diminishes in every direction inversely as the square of the distance; but it is quite otherwise if the charged ball be suspended within the hollow sphere in any other position. If we compare radiant heat

with induced electricity, it will be found that the approach of a cold body, S, towards a source of radiant heat does not affect the radiation to the objects around, excepting in the case of those which are immediately sheltered by its shadow, as at B, fig. 184; not so, however, if we bring an uninsulated conductor towards a body charged with electricity. The approach of such a conductor concentrates the inductive action more or less completely upon itself, and to a corresponding extent withdraws that action which was previously directed towards the surrounding, but more distant, envelope. The fewer are the intervening particles of the dielectric air to be polarized, the higher does the polarity rise in each particle, and the more completely is the induction called off from more distant objects; consequently the smaller the distance between the charged and the disturbing body, the more complete is the diversion. The polarity of the interposed air may at last rise so high that it can sustain the tension no longer, and a spark passes between the two surfaces. The particles of the dielectric are in a strained condition, and, like the coils of a spring, tend to return to their normal state.

Fig. 184.

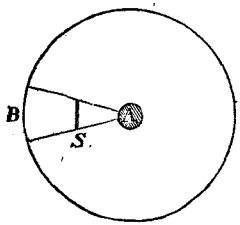
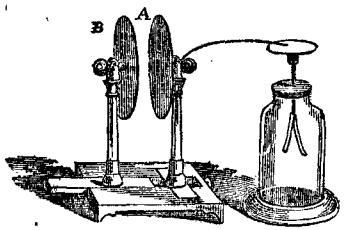


Fig. 185.

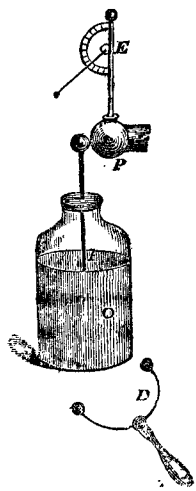


This important fact may be illustrated in the following way. Let A, fig. 185, represent an insulated circular conducting plate connected with an electroscope. Give to the plate A a small positive charge sufficient to cause divergence of the leaves of the electroscope; then cause a second conducting plate, B, which is uninsulated, to approach the plate A. The leaves of the electroscope will gradually collapse, but they will open out again, when B is withdrawn. In this experiment a portion of the positive electricity of plate B, equivalent in quantity to that of the charged body, A, passes off to the earth. Owing to this lateral action, if the plate B be retained very near to A, the plate A may receive a considerable charge, by repeated applications of a body feebly charged, provided that such body is freshly charged between each contact with A: by these repetitions small quantities of electricity may be accumulated, and rendered evident by withdrawing the uninsulated plate, B; the leaves

of the electroscope diverge, because by such withdrawal the whole induction is directed to surrounding objects instead of being concentrated upon B. An apparatus of this kind has been called a *condenser*, from its power of collecting and rendering visible, by repeated contacts, quantities of electricity too minute to be otherwise perceptible.

(235) *The Leyden Jar.*—By substituting a solid dielectric, such as glass, for the sheet of air between the plates A and B in the preceding experiment, a much higher degree of induction may be obtained, since the fixed position of the particles of the glass prevents them from moving off when highly charged. In fact, a plate of glass between two metallic surfaces constitutes an apparatus for storing up electricity; and is, in its simplest form, the important instrument celebrated from the place of its discovery as the *Leyden Jar*. Excepting as a matter of convenience it does not signify whether the glass be flat or curved, only it is found more easy to manipulate with jars than with flat plates. The ordinary form of Leyden jar is represented at O, fig. 186. It consists of a bottle, of thin glass, with a wide neck. A coating of tinfoil is pasted upon both the internal surface I, and the outer surface, O, to within three or four inches (8 or 10 centimetres) of the neck. The upper portion of the glass is left free from conducting matter in order to preserve the insulation of the two coatings. A wire, surmounted by a brass knob, and supported by a smooth plug of dry wood, serves to convey the charge to the inner coating, with which it is in contact. Such a jar will receive and sustain a much larger charge than a simple conducting surface of brass or of tinfoil of the same extent.

FIG. 186.



A simple experiment will suffice to show the correctness of this statement. A single turn of the machine will be sufficient to cause a straw, E, fig. 186, suspended from the centre of the graduated arc, and attached to the prime conductor of the machine, P, to assume its utmost angular repulsion; but if the knob of a Leyden jar, which need not expose a coated surface of an extent equal to the superficial area of the prime conductor, be presented as at P, it will take eight or ten turns of the machine to produce the same amount of repulsion; bright sparks will pass in rapid succession between the knob and the

conductor, if the two be separated by a small interval, and on connecting the two coatings of the jar by the *discharging rod* D (which is merely a jointed wire terminating in brass balls, and which for safety is insulated on a glass handle), the equilibrium is restored suddenly and completely with a loud snap and a brilliant spark. If the discharge were allowed to take place through the arms, or any part of the body, a sudden painful sensation, termed the *electric shock*, would be experienced. The power of the Leyden jar may be increased by increasing its size; and when it would be inconvenient to use jars of large size, a similar increase in power may be obtained by placing a number of small jars side by side upon a sheet of tinfoil, or other conductor, which connects together all their outer coatings, whilst by means of wires all their inner coatings are similarly connected with each other. Such an arrangement of jars is called an *electrical battery*, and is shown at fig. 197. If the jars be of uniform thickness, the energy of the battery will be in proportion to the extent of the coated surface, and inversely as the thickness of the glass. (Wheatstone, *Government Report on Electric Cables*, 1861, Appendix, p. 285.)

That the charge of the Leyden jar depends upon an action of contiguous particles, polarization taking place across the dielectric, may be shown by taking three or four laminæ of glass, and placing them one above another between two metallic plates, thus forming them into one compound plate, and then charging the whole. If the upper plate becomes positively charged, the lower one will become negative, whilst each intermediate plate becomes polarized, and thus transmits the inductive effect.

As might be anticipated from this experiment, it is found that the charge of the jar does not reside in the coatings, which merely act as conductors to favour the distribution and escape of the electricity. If a jar be fitted with moveable coatings, and then charged, each of the coatings may be removed by a suitable insulating support; the coatings may be handled after such removal; the jar may then be replaced in them, and it will give a powerful spark when discharged in the usual manner.*

The following experiments will elucidate the action of the

* The jar, if well dried, will be found after this discharge still to retain a polar condition like the cake of the electrophorus. After the discharge, if the inner coating be withdrawn by an insulating handle, it will give off a positive spark, and, on replacing the coating, the jar may be a second time discharged; and the same series of operations may be repeated several times.

Leyden jar when in the process of receiving a charge. Let a jar, A, fig. 187, be placed upon an insulating stand, and let its knob be brought near to the prime conductor, P, of an electrical machine in action; under these circumstances it will be found to receive little or no charge. Now place an uninsulated conductor, C, near its outer coating: sparks will pass from P to the knob of the jar A; and for every spark that passes to the knob of the jar, a spark will pass from the outer coating to the uninsulated conductor, C. If the jar be receiving positive electricity from the machine upon its interior, it will be found that an equal quantity of positive electricity is disengaged from the exterior. A second uninsulated jar may be placed so as to receive upon its knob the sparks from the exterior of the first; it will thus become charged to an extent equal to the charge of the first jar. Again, if three insulated jars be placed as in fig. 188,

FIG. 187.

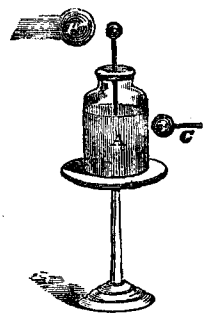
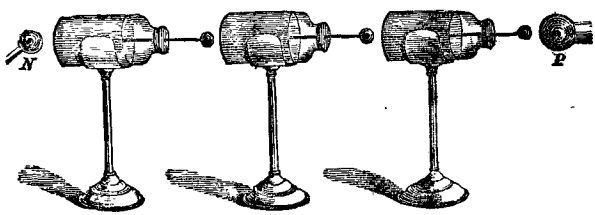


FIG. 188.

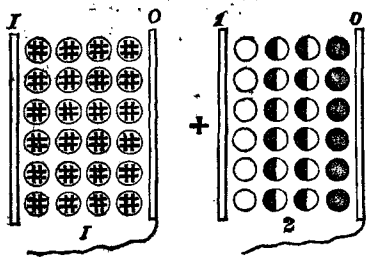


where P indicates the prime conductor, whilst the coating of the last jar is brought near to a wire, N, proceeding from the insulated rubber of the machine, for each spark that passes from the conductor, P, a similar spark will be seen to pass between each of the jars, and between the last jar and the wire, N. In this way each jar will become powerfully and nearly equally charged, although both the machine and the jars are completely insulated.

From the foregoing experiments it is plain that a jar when charged contains no more of either electricity than it does in its neutral condition, but the distribution of the electrification is different. This statement may be illustrated by aid of the diagram, fig. 189:—Let No. 1 indicate an enlarged section of the glass side of the jar, the partially shaded circles showing its particles in the neutral state; I representing a section of the inner metallic coating, and O a section of the outer coating. Let

No. 2 be a section of the same jar when a charge of positive electricity has been thrown by the machine upon the inner surface, 1. In this case a corresponding quantity of negative electricity must have passed off from the same coating to the conductor of the machine, leaving the superficial layer of particles apparently charged with positive electricity, as shown by the white circles in No. 2. In order, however, that this charge of the inner layer may occur, it is necessary that the outer layer be uninsulated, for reasons which will be immediately explained. The two electricities in No. 2 are represented as being accumulated on opposite sides of each of the particles composing the layers intermediate between the inner and outer superficial layers of the glass, the white half indicating the positive electricity, the black half the negative. Polarization of each particle of the dielectric glass intervening between the two surfaces is produced, and a quantity of positive electricity is therefore disengaged from the second surface, which is exactly equal to that distributed by the inner coating, 1, upon the first; but unless an escape be afforded for this excess of positive electricity from the second surface, no charge is received by the jar, for polarization becomes impossible, and no appreciable amount of electricity can enter the jar from the machine. At the same time that positive electricity is escaping from the outer superficial layer, a corresponding quantity of negative electricity supplies its place, consequently this layer becomes apparently charged with negative electricity, as indicated by the fully shaded circles.

Fig. 189.



It thus appears that the operation of charging a jar with electricity is totally different from that of filling a bottle with a liquid; the electricity is distributed, not in the cavity of the bottle, but in the substance of the glass itself. Indeed, it has been already stated that a flat plate will answer equally well with the jar, but the jar, from its form, is for the sake of convenience preferred. In the experiment with the three insulated jars, an explanation similar to the foregoing one may be given:— A quantity of positive electricity passes from the conductor of the machine to the inner surface of the first jar. A corresponding quantity of the same kind of electricity passes off simulta-

neously from the opposite coating into the next jar, which in its turn becomes similarly polarized; and so on in succession, until, from the last jar, a quantity of positive electricity passes to the rubber, exactly sufficient to neutralize the negative electricity liberated by the machine, which is necessarily equivalent to the positive electricity accumulated on the internal surface of the first jar. It is not necessary that the last jar be connected with the rubber directly; the same object will be attained by allowing the discharge to take place into the earth, provided that the rubber also be in conducting communication with the earth. Although it is usual in the charging of a jar to connect the internal coating with the prime conductor, yet the jar may be charged equally well if its insulated *external* coating be connected with the conductor whilst the inner coating is made to communicate with the earth; in this case, however, the charge on the outer surface is positive, whilst the inner surface becomes negative.

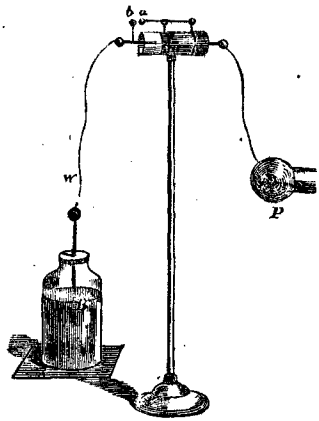
Each jar in the series, fig. 188, thus receives a charge, though only one has been placed in connexion with the machine; the superfluous electricity upon the outer coating of the first having charged the second, and so on. If the insulations be good, and the glass of the jars thin, the last jar will be charged very nearly to the same extent as the first.

When all the jars have been thus charged, all will be simultaneously discharged if the inner coating of the first jar be connected with the outer coating of the last; but although no greater amount of electricity passes between the two extreme jars than would have passed between the inner and outer coating of a single one, the distance through which the spark passes is very much greater, and for equal charges it is found to increase as the number of jars thus discharged: if a spark of one centimetre in length be obtained with one jar, with two jars the spark would be two centimetres, with four four centimetres, and so on. In practice the distance is something less, because, owing to imperfect insulation and to the resistance of the glass to receive a charge, each succeeding jar receives a charge somewhat weaker than the one which precedes it.

(236) *Measures of Electricity.*—It is upon the principles just explained that Snow Harris constructed his *Unit jar*, for measuring out definite quantities of electricity. The unit jar is a miniature Leyden jar mounted on a slender insulating rod of glass. Attached to the outside of the jar is a wire terminating in a ball, *a*, fig. 190, parallel to the usual wire and ball which passes to the interior; on the wire connected with the inside is a third sliding ball, *b*; this can at pleasure be brought to any required distance from the ball, *a*, which is connected

with the outside: whilst the unit jar is becoming charged from the machine (say that its outer surface is rendered positive, as represented in the figure), an equal quantity of positive electricity is passing off from the interior along the wire, *w*, attached to the inside of the jar, B, which is to be loaded with a definite quantity, the interior of the small jar becoming negatively charged by induction: as soon as the negative charge in the unit measure rises sufficiently high, it discharges itself between the adjusted balls, *a*, *b*, without affecting the charge in the jar, B. A second charge is now given to the unit jar, which discharges itself when it rises to the same amount as before: during each successive charge of the unit jar, a corresponding quantity of positive electricity passes from its exterior into B, so that by counting the number of sparks that pass between *a* and *b*, the number of equal quantities or arbitrary units which have been given to the jar, B, is ascertained. Supposing the adjustment of the balls, *a* and *b*, to remain the same, the jar B may be made to receive, for any number of times successively, equal amounts of electrical charge, by causing an equal number of discharges of the unit jar to take place in each case.

FIG. 190.



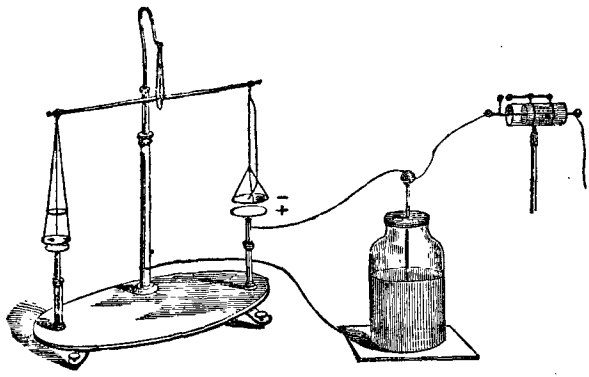
Other means have been proposed for ensuring an equal accumulation of electricity in a jar. *Lane's discharging electrometer* is the simplest of these. One form of this apparatus is shown in fig. 191: its principle of action will be at once apparent. L is an ordinary Leyden jar, in the ball A of which a hole is drilled to receive the brass pin of the electrometer; a bent glass arm, *b*, carries upon its lower extremity a brass socket, *c*, through which slides an insulated rod carrying a brass knob on either extremity; one of these balls, *f*, can be placed at any required distance from the knob of the Leyden jar. A chain or wire, *w*, effects a communication between the sliding rod and the outside of the jar. If the interval between A and *f* be maintained the same, the jar will always require the same amount of charge before the discharge takes place between these two balls, A, and *f*. The quantity of electricity in the charge is proportional to the distance between the balls: with an interval of 10 millimetres the quantity would be double that required when the distance was only 5 millimetres.

FIG. 191.

The attraction between two charged surfaces has been measured by an ingenious modification of the common balance devised by Snow Harris. A light disk of gilt wood is substituted, as shown in fig. 192, for one of the pans of the balance; beneath it is a second similar insulated disk: the suspended disk and the balance beam, through its support, are connected with the exterior of a Leyden jar, and the lower insulated disk with the interior of the jar. By charging the Leyden jar with definite quantities of

electricity by means of the unit jar, the laws which regulate the attraction were experimentally determined. One or two of the more important results may be given as an illustration of the mode of proceeding.

FIG. 192.



If a Leyden jar charged with a certain quantity of electricity produce between the disks an attraction sufficient to support 0·2 grm., it will when charged with double the quantity support four times the amount, or 0·8 grm.; with three times the quantity it will raise nine times the amount, or 1·8 grms.; consequently, if the extent of charged surface continue constant, the attraction increases as the square of the quantity.

When two equal and similar jars are used instead of one jar, and the same quantity, say ten units, is distributed over them, the attraction will be diminished to $\frac{1}{4}$, and with three jars to $\frac{1}{9}$ of what it was when a single jar was employed. For instance, a quantity which on one jar would support 1·8 grms., would, if diffused over two similar jars, support only 0·45 grm.; and if diffused over three, it would support only 0·2 grm. If, therefore, the quantity remain constant, the attraction is inversely as the squares of the charged surfaces of the jars. When the distance between the disks was altered, it was found, for charges of equal superficial density, that the attraction varied inversely as the square of the distance,—the attraction being 4 times as great at a distance of 1 centimetre as it was at 2 centimetres.

(237) *Specific Induction.*—It has been shown that the induction between two conducting plates, one of which is insulated while the other communicates with the earth, is facilitated by diminishing the thickness of the dielectric which separates them, and that the insulated plate is enabled to receive a higher amount of charge by reducing the number of particles of the dielectric

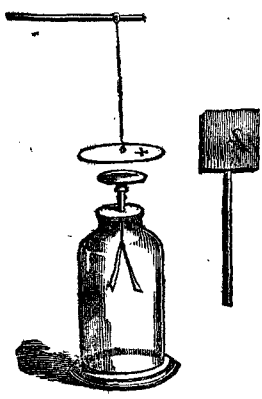
which undergo polarization. It is evident from this circumstance that the polarization is attended with a certain amount of resistance. Faraday discovered that this resistance varies in amount with the material of the dielectric employed; some substances becoming polarized more readily than others. The relative facility of induction through the different bodies as compared with a common standard constitutes their *specific inductive capacity*. A plate of shell-lac, for example, of a centimetre in thickness, allows induction to take place across it twice as readily as does an equal thickness of atmospheric air, and sulphur with a facility equal to that of shell-lac.

The following Table represents, according to Snow Harris (*Phil. Trans.* 1842, 170), the specific inductive capacity of various bodies:—

Specific Inductive Capacity.

Air	1·00	Glass...	1·90
Resin...	1·77	Sulphur	1·93
Pitch	1·80	Shell-lac	1·95
Bees'-wax	1·86		

FIG. 193.



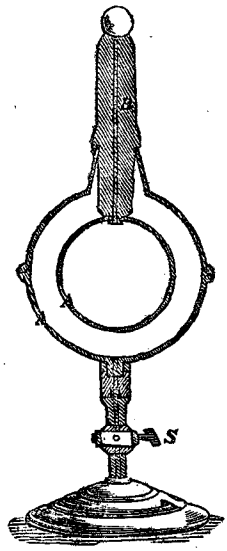
The fundamental fact may be shown by the following simple experiment (fig. 193). About 1½ inch, or 4 centimetres above the cap of a gold-leaf electroscope suspend an insulated disk of metal, and communicate a small charge to the insulated disk; the gold-leaves immediately diverge by induction. Between the disk and the electroscope substitute for the dielectric air, a body the specific induction of which is greater than that of air, such, for example, as a plate of shell-lac, S, an inch (25 millimetres) in thickness, and mounted on an insulating handle; the leaves will immediately diverge more widely, because induction towards the instrument takes place more freely; on removing the shell-lac the leaves of the electroscope return to their original divergence. The effect is precisely similar to that which would be produced by bringing the charged plate nearer to the electroscope in air. Similar phenomena occur if a mass of sulphur or of resin is substituted for the shell-lac.

In good conductors no such polarization can be traced, and in imperfect conductors, such as spermaceti, the results become indistinct.

With gaseous bodies no difference in specific inductive capacity is found to exist; it is remarkable that the chemical nature of the gas has no influence; all gases having the same inductive capacity as common air. No variation in temperature, in density, in dryness, or in moisture, produces any change in this respect.

The apparatus with which Faraday investigated these curious phenomena was a kind of Leyden phial (fig. 194), consisting of two concentric metallic spheres, A, A, insulated from each other by a stem of shell-lac, B. Any dielectric could in succession be placed between the spheres, whether the subject of experiment were solid, liquid, or aëriform, as by connecting it with the air-pump by means of the stop-cock, S, it could be exhausted, and the interval filled with any gaseous medium, with the same facility as with a liquid (*Phil. Trans.* 1838, 9). Two of these jars having been prepared, a charge was given to one of them, after it had been filled with the body the inductive capacity of which was to be determined, and the charge was then divided with the second similar apparatus, in which the interval between the spheres was filled with air only. The charge in each case was measured by means of a carrier-ball and Coulomb's electrometer.

FIG. 194.



(238) *Various Modes of Discharge.*—We pass on now to consider the different modes in which the electric equilibrium is restored after it has been disturbed: this restoration may be effected in one of three ways, for the excited body may be discharged either by (*a*) *conduction*, by (*b*) *disruption*, or by (*c*) *convection*.

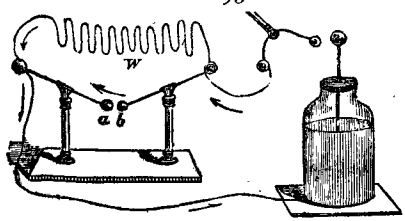
(239) *a. Conduction.*—When a charged Leyden jar is discharged in the usual way through a discharging-rod, the electricity passes quietly through the wire of the discharger by conduction, but traverses the interposed air by disruption, in the form of a spark attended with noise.

All bodies, shell-lac and glass not excepted, possess a certain amount of conductivity, which gives rise to the phenomenon termed the *residual charge* of a jar or battery. If a jar be charged strongly, and allowed to remain undisturbed for a few minutes, and then be discharged and again allowed to stand for a few moments, a slight apparent renewal of the charge will take place, and a second smaller spark may be obtained from it. This Faraday considers to be due to the penetration by conduction of a portion of the charge into the substance of the dielectric. Each surface of the glass acquires a weak charge, one of positive, the other of negative electricity; but as soon as the constraint which caused this penetration of the electricity is removed, it returns towards the nearest surface and produces the slight recharge, or residual charge.

As no bodies are perfect insulators, so none are perfect conductors, for even the metals offer a certain measurable resistance

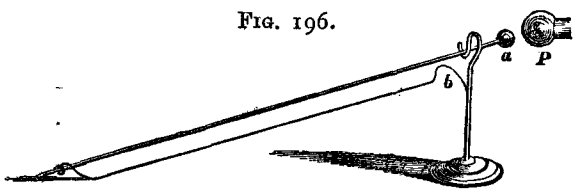
to the transmission of electricity. The following experiment will serve to illustrate this point. Charge a large Leyden jar (fig. 195), and arrange a metallic wire, w, from 120 to 150 feet, or 40 or 50 metres in length, so as to act the part of a discharger; at the same time open a short path for the discharge to the outer coating, by bringing the balls *a* and *b* within a short distance of each other. Under this arrangement, a portion of the electricity takes the shorter course from *a* to *b*, and overcomes the high resistance of the stratum of air interposed between the balls, owing to the resistance experienced by the discharge to its passage along the continuous conducting wire, *w*.

FIG. 195.



This resistance, even in good conductors, often occasions the spark to pass between two contiguous conductors, and produces what has been called the *lateral spark*, which can be elicited, even if the conductors subsequently unite below. For example, in the arrangement shown in fig. 196, at the moment a spark

FIG. 196.



passes from P to the ball, *a*, a minute spark will be seen to pass between the wire and the loop, *b*, if they be sufficiently near each other. This lateral spark may acquire sufficient power to ignite gunpowder or other combustible matter. In fact, momentary as is the duration of the discharge, induction takes place towards all surrounding objects whilst electricity is in motion, as well as when it is at rest.

If in a darkened room a thin insulated wire be made to terminate at each extremity in a metallic ball, and on one ball large sparks be thrown, whilst from the other ball the sparks are allowed to pass off to some contiguous conductor, the air will be seen to become feebly luminous from induction along the whole course of the wire every time that a spark passes.

(240) *Development of Heat.*—The passage of electricity through conductors is attended with evolution of heat, the amount of which

is inversely as the conducting power. Snow Harris (*Phil. Trans.* 1827, 21), by means of an air-thermometer with a large bulb, across which were passed in succession wires of different metals but of equal length and thickness, found that when equal quantities of electricity were discharged through these wires, the heating effects were as follows. The metals which stand first on the list are the best conductors, and they emit the least heat:—

Development of Heat in Metals by Electricity.

		Alloys.	
Copper	6	Brass	18
Silver...	6	Gold 3, Copper 1	25
Gold	9	Gold 1, Copper 3	15
Zinc	18	Gold 3, Silver 1	25
Platinum	30	Tin 1, Lead 1	54
Iron	30	Tin 1, Copper 8	18
Tin	36		
Lead	72		

It will be seen that by alloying the metals with each other, the conductivity is often greatly reduced. Great care should therefore be taken to ensure the purity of the metals in experiments of this nature.

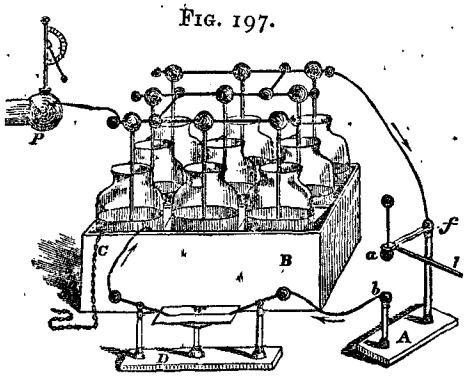
If different quantities of electricity be transmitted through the same wire, it is found that the rise of temperature is proportional to the square of the quantity transmitted in equal times: for example, if the thermometer, with a given charge, rise 10°, a charge of twice the power will raise it four times as much, or 40°.

By sufficiently reducing the thickness of the conductor at one part of the circuit, the heat may be raised so far as to fuse the wire, or even to convert it into vapour.

The amount of electricity required to produce this effect, when measured by a unit jar, is found to be equally powerful, whether it be diffused over a large or small surface; the *intensity* (*i.e.* quantity which passes through a given space in a given time) is the same in the wire in both cases, though the density of the charge on equal surfaces of the jar is very different. Where large quantities of electricity are needed, a corresponding extent of coated surface is requisite; this may be obtained either by employing a single jar of large dimensions, or several smaller ones, the inner surfaces of which are connected by wires, and the outer surfaces likewise united by placing them upon a sheet of tinfoil, or on a metallic tray. By discharging such a battery through thin metallic wires—of silver, steel, platinum, or copper, for instance—they will be fused and dispersed.

The arrangement represented in fig. 197 shows one method of employing such a battery for the deflagration of metallic wires: nine jars are in this case represented; they are enclosed in a wooden case, B, and rest on tinfoil, which communicates with the earth through the chain C. The battery is charged from the prime conductor P. The internal coatings of all the jars are connected by cross wires. In order to direct the discharge of the battery, a wire passes from its inner coating to the insulated upper arm, *f*, of the discharger A; a second wire passes from the ball *b*, to one of the insulated wires on the stand of the *universal discharger* D. The wire for deflagration, *w*, is fastened to a card which is also supported on a little stand insulated by glass; and the communication with the external coating of the battery is continued by a wire connected with the other insulated support of the universal discharger D; thus the conducting communication is complete with the exception of the interval between *a* and *b*. When the battery is adequately charged, the lever *l* is withdrawn, the ball *a* and its attached wire are thus released, and fall through a hole in the metallic arm *f*, which is connected with the inner coating, and the circuit is completed when the balls *a* and *b* come into contact.

Fig. 197.



It must be observed that in all cases of conduction the charge passes through the whole thickness of the rod or wire, and is not confined to its surface: it therefore makes no difference whether the metal is in the form of wire, or is extended over a large surface as leaf. The induction at any part of the wire during the discharge is mainly from one transverse section of the wire to the contiguous section that immediately precedes and that follows it.

The dispersion of the conductor by the passage of high charges of electricity leads us to consider next what Faraday has termed the *disruptive* discharge.

(241) *b. Disruptive Discharge.*—This mode of discharge is attended by sudden and forcible separation of the particles of the medium through which it occurs; and it is attended with evolution of light and heat. It is best seen between two conductors separated by a dielectric, such as two metallic balls in air. In these cases, when a sudden bright spark passes, the discharge is as complete as if it had been effected by direct metallic communication. The particles of the intervening dielectric are brought up to a highly polarized state, until at length the tension on one particle rising higher than the rest, and exceeding that

which it can sustain, it breaks down: the balance of induction is thus destroyed, and the discharge is completed in the line of least resistance.

In all these cases, portions of the solid conductors are detached, and by their ignition increase the brilliancy of the spark. This transfer of material particles by the spark is easily proved, for if sparks be caused to pass between a gold and a silver ball, the surface of the gold becomes studded with particles of silver, and *vice versâ*. If an iron chain be laid on a sheet of white paper, and a powerful discharge be sent through it, each link will leave upon the paper a stain, arising from the portions of the metal which have been detached: and if the discharge be effected over a plate of glass, particles of the metal are frequently forced into it. The experiment may be varied by suspending the chain in a dark room, and passing the discharge through it; brilliant deflagration of the iron will be seen at each link.

If the sparks be taken between wires composed of different metals, and the light of each spark be viewed through a prism, the spectrum will in each case exhibit the bright lines due to the light of the corresponding metal in the state of vapour (106).

Sparks attended with disruption may also take place in the midst of liquid dielectrics. More rarely disruption from the discharge occurs in solids: occasionally this is exemplified in the Leyden jar itself, the tension upon the glass now and then rising so high that the glass becomes perforated. Across this fracture discharge always afterwards occurs; so that no effective charge in a battery can be maintained till the cracked jar is removed. This disruption of glass may be produced at pleasure by bending a wire so that its point may press against the side of a tube or other vessel filled with some liquid dielectric, such as olive-oil. On charging the wire from the prime conductor, and applying a ball to the outside of the tube opposite the end of the wire, a spark passes, and a minute perforation is produced.

Great expansion of the air occurs from the heat developed at the moment of the discharge, as is shown in the following experiments. Paste a strip of tinfoil on glass, cutting it through in two or three places with a knife; place a few wafers or other light bodies over the interrupted points, then discharge a jar through the tinfoil, and the wafers will be immediately scattered in all directions. If a card or half quire of paper be placed in the direction of its thickness in the track of the discharge, the card or the paper will be burst outwards on both sides.

Many pleasing experiments may be made by causing a succes-

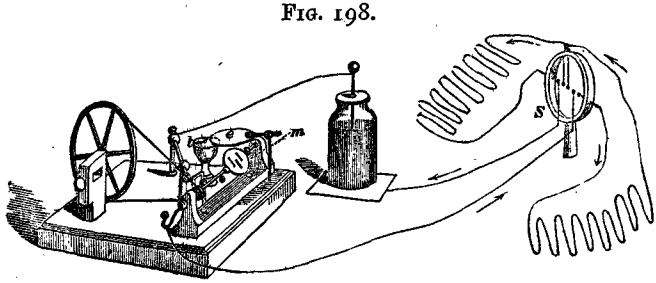
sion of discharges to occur through such interrupted conductors; a beautiful display of the electric light may thus be exhibited in a darkened room.

(242) *Velocity of Discharge.*—Of the velocity of the spark discharge some notion may be formed from the brief duration of its light, which cannot illuminate any moving object in two successive positions, however rapid its motion. If a wheel be thrown into rapid rotation on its axis, none of its spokes will be visible in daylight, but if the revolving wheel be illuminated in a darkened room by the discharge of a Leyden jar, every part of it will be rendered as distinctly visible as though it were at rest. In a similar manner, the trees even when agitated by the wind in a violent storm, if illuminated at night by a flash of lightning, appear to be absolutely motionless.

By a very ingenious application of this principle, Wheatstone has shown that the duration of the spark is less than the one-millionth part of a second. The apparatus is the same in principle as the revolving wheel.

By a modification of the apparatus, Wheatstone was also enabled to measure the velocity with which the discharge of a Leyden jar was transmitted through an insulated copper wire. He estimated the rate of its passage at 288,000 miles in a second (*Phil. Trans.* 1834, 589). For this purpose he employed an insulated copper wire about half a mile long, through which a Leyden jar was discharged. This insulated circuit was interrupted at three points; one of these interruptions was within a few metres of the inner coating of the Leyden jar; the second was in the middle of the wire; and the third within a few metres of the outer coating of the jar. The parts of the wire at which these three breaks in the circuit occurred were all arranged side by side on an insulated disk, so that the three sparks could be seen simultaneously. In fig. 198 a wire is represented

FIG. 198.



as proceeding from the knob of the jar to an insulated rod; when the charge attains a certain tension, a spark passes between this rod and a small knob attached to the axis of a small revolving mirror, *m*: to one extremity of this axis, the wire which passes to the outer coating is fastened; but the discharge is made to traverse the whole length of the two intervening long contorted portions of wire before it reaches the outside of the jar. The three sparks, if viewed by the naked eye, appear to be simultaneous. If viewed through the glass plate, *e*,

in a small steel mirror, *m*, to which is given a regulated but extremely rapid revolving motion on an axis parallel to its surface, the sparks appear no longer as dots of light in the same horizontal line, but present the appearance of three bright lines of equal length. The two outer ones commence and terminate in the same horizontal line, but the middle one occurs later than the other two, and the angular position of the mirror has had time to advance slightly before the middle spark appears, which consequently exhibits an image slightly displaced. As the velocity of rotation of the mirror is recorded by the register, *b*, and the amount of this angular deviation of the image of the central spark is easily ascertained, the retardation of the discharge by the copper wire, or, in other words, the velocity with which it travels along it, can be estimated.

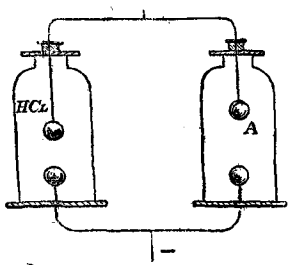
This experiment has another important signification, to which due weight appears hardly to have been given; for it affords a convincing proof of simultaneous action and reaction in the operations of electricity, and of its existence as a stress: at the same moment that a positive influence leaves the inner coating, an equal amount of negative influence leaves the outer coating, and these two neutralize each other at the central point of the conductor, after the lapse of an extremely minute but still appreciable interval of time. It appears from this experiment that Franklin's theory (227), though in many cases a simple and convenient mode of explaining facts, is not the true representation of the phenomena. The theory of two fluids seems by this experiment to be demonstrated.

The velocity of the electric discharge is, however, found to vary with the intensity of the charge, and with the nature of the conducting medium (Faraday, *Phil. Mag.*, 1854, [4] vii., 197). The duration of the discharge may be prolonged by causing it to take place through bodies of inferior conducting powers. A charge of a given amount, if transmitted slowly, may, by the prolonged period through which its heating powers can be applied to a combustible, be made to ignite bodies, which the same charge, if more quickly transmitted, would only have dispersed. For example, let two metallic wires be brought within an eighth of an inch ($3^{mm.}$) of each other, and let a little loose gunpowder be placed over the interval—the powder will simply be dispersed if the charge of a Leyden jar be sent through the wires; but if a few inches of wet string be interposed in any part of the circuit, the discharge will be prolonged sufficiently to fire the powder.

(243) *Striking Distance.*—In air, whatever be its density, the same charge produces, *cæteris paribus*, induction to the same extent. But the distance through which the discharge of equal quantities of electricity takes place in the same gaseous medium, varies inversely as the pressure. This might be anticipated, since under a double pressure double the number of particles of air

would exist in the same space, and the polarity would therefore be transmitted through double the quantity of insulating matter: —so that, if a given charge in air of ordinary density pass as a spark at 2 centimetres, at double the usual pressure the striking distance would be reduced to 1 centimetre; at a pressure of one-half it would be increased to 4 centim.; at one quarter, to 8 centim.; and so on, until *in vacuo* theoretically it would pass through an unlimited distance. Experiment, however, has shown that a certain portion of matter, though it may be attenuated to an extent almost beyond the limits of calculation, is necessary for the transmission of the electric discharge (312). If the density of the air continue to be constant, it is found that the striking distance varies directly as the tension of the charge. For example: if with a certain charge the striking distance be 1 centimetre, a double charge will discharge itself through 2 centim., and a three-fold charge through 3 centim. (Harris.) For equal quantities of electricity the striking distance is inversely as the extent of charged surface; so that, when a single jar is charged with a quantity of electricity sufficient to produce a discharge at $6^{mm.}$, on employing two similar jars with the same quantity, the striking distance is reduced to $3^{mm.}$, and with three similar jars to $2^{mm.}$ For equal charges, the striking distance, however, varies in different gases, independently of their relative density, so that each gas has a specific insulating power. Hydrochloric acid has twice the insulating power of common air, and three times that of hydrogen of equal pressure. This is in striking contrast to the equality of inductive capacity (237) in all gases.

FIG. 199.



This inequality of insulating power was proved by Faraday by opening to the same charge two separate paths, one of them through air, the other through a receiver filled with the gas which was to form the subject of the experiment, as shown in fig. 199. The distances between the balls were varied until the discharge took place with equal facility in both receivers; the same charge was thus found to traverse double the distance in air that it did in hydrochloric acid gas.

Rarefaction of air, whether effected by heat or by mechanical means, equally favours the electric discharge. A jar may consequently be discharged through several centimetres of a common flame, in which the air is rarefied by heat to nearly five times its ordinary bulk, the temperature of an alcohol flame, ac-

cording to Becquerel's experiments, being nearly 2200° (1204° C.). A flame also acts by its pointed form in dissipating a charge with great rapidity, and its proximity should be avoided in exact experiments.

Dissipation of the electric charge in dry air, according to Matteucci, is not increased by agitation of the air. Further, if the gases are all perfectly dry, and at the same temperature and pressure, the dissipation of the charge takes place with equal rapidity in air, in carbonic anhydride, and in hydrogen. In a moist atmosphere the loss of charge increases directly, *cæteris paribus*, as the amount of moisture. As the temperature rises, the dissipation of the charge increases in rapidity, the loss of the charge being twice as rapid at 18° as at 0° C. If the density of the air be reduced, the tension of the charge which an insulated body will retain is reduced also, but the dissipation of the charge is very much diminished. Matteucci found, when an electroscope, feebly charged, was placed in a receiver, exhausted till the pressure was reduced to $3^{mm.}$ of mercury ($\frac{1}{8}$-inch), that the divergence remained unaltered after a lapse of two days.

The form and size of the spark depend upon the shape of the discharging surfaces almost as much as upon the intensity of the charge. Between the rounded parts of the prime conductor and a large uninsulated metallic ball dense brilliant sparks pass; whilst if the same ball be presented to a wire which projects 8 or 10 centimetres from the conductor, and which terminates in a ball $25^{mm.}$ or an inch in diameter, a long, forked, and often branching spark, resembling a miniature flash of lightning, will be obtained.

When disruptive discharge occurs between a good conductor of limited surface and a bad one which exposes a larger surface, an intermitting and dilute spark or *brush* passes, which, when it occurs in air, consists of a rapid succession of discharges to the particles of air around: such a brush has a bright root with pale ramifications, attended with a quivering motion and a subdued roaring noise. Brushes of this kind are well seen when, the machine being in powerful action, the conductor is made to discharge itself into the air by means of a blunt rod which projects from it. The brush is largest from a positively charged surface, such as the prime conductor of the machine. From a negatively charged surface this discharge occurs at a lower tension, and more resembles a bright point or star of light. The formation of brushes is facilitated by rarefying the air around the charged points.

Some remarkable differences have been observed between the positive and the negative spark: for a charge of equal tension, the striking distance, between a good conductor positively charged and an inferior conductor, is greater in air than from the same conductor negatively charged, as may be seen in using the electrophorus. The greater facility with which positive electricity traverses the air may also be shown in the following manner:—Colour a card with vermilion; unscrew the balls, *a*, *b*, from the discharger, fig. 197, and place the points on opposite sides of the card, one about half an inch ($12^{mm.}$) above the other; discharge a large jar through the card. It will be perforated opposite the wire attached to the negative coating, and an irregular dark line of reduced mercury will be found extending on the positive side to the point of the positive wire. If the experiment be made *in vacuo*, the perforation will be formed midway between the two wires. The distinction between positive and negative electricity is also beautifully shown by what are termed Lichtenberg's figures, which may be obtained as follows:—Dry a glass plate, and draw lines on it with the knob of a positively charged jar, then sift over the plate a mixture of sulphur and minium in fine powder: on inverting the plate the minium will fall off and leave traces of the lines in sulphur. If the experiment be made with a jar negatively charged, the minium will adhere to the traces, whilst the sulphur will fall off. The explanation is very simple: by the friction in sifting, the sulphur becomes negatively, the red lead positively electric, and thus the sulphur attaches itself to the positively electrified lines upon the glass, and the minium to the negatively electrified lines, in accordance with the usual law of electric attraction. The experiment may also be varied in the following way:—Take two circular trays of tin-plate half an inch ($12^{mm.}$) deep and 12 or 14 inches (30 or 35 centimetres) in diameter, fill them with melted resin, and allow them to cool; cause sparks of positive electricity to fall in 8 or 10 places upon one plate, and sparks of negative electricity in like manner over the other; on sifting a little brickdust over the two plates, the dry powder will assume the appearance of brushes over the plate electrified positively, and of oval or circular patches upon the negatively excited plate. Other remarkable differences between the sparks from positive and negative surfaces will be mentioned when noticing the modified discharges through exhausted tubes (312).

The colour, light, and sound of the electric spark and brush vary in different gases (106), the brush being larger and more beautiful in nitrogen than in any other gas, and its colour is purple or bluish. The sparks in oxygen are whiter than in air, but less brilliant. In hydrogen they are of a fine crimson colour. In coal-gas they are sometimes green and sometimes red; occasionally both colours are seen in different portions of the same spark. In carbonic anhydride the sparks resemble those taken in air, but they are more irregular and pass more freely.

(244) *c. Convection.*—With a feebler charge the sonorous brush is replaced by a quiet glow, attended in this case with a continuous dispersion of the charge. The process of disruptive discharge thus gradually passes into the third method—viz., that by *convection*. When the glow is produced, a current of air, the particles of which are individually charged, passes from the charging surface. The course of this current may be exhibited by its

action on the flame of a taper, which will often be extinguished if brought near an electrified point which is connected with the machine in action; and light models may be set in motion by it. If the production of the current from the point be prevented, as by sheltering the pointed wire in a varnished glass tube, the brush or glow may be converted into a series of small sparks. These currents may take place in liquid dielectrics as well as in gaseous ones. Let a piece of sealing-wax be fixed on the end of a wire and attached to the conductor of a machine in action; if it be softened by the application of the flame of a spirit-lamp, it will be thrown off in filaments towards a sheet of paper held near it. Solid insulated particles may also be the medium of convective discharge, as is seen when pith-balls or other light substances are attracted and repelled by electrified objects; and in delicate experiments even the particles of dust floating in the atmosphere are not without effect in charging or discharging the apparatus employed.

The process of convection assumes considerable importance in the phenomena of voltaic electricity, where it is intimately connected with chemical decomposition. (281 *et seq.*)

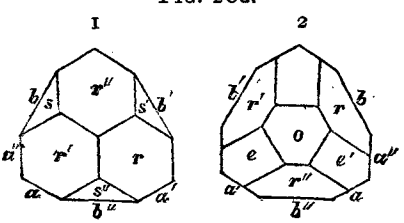
(245) *Other Sources of Electricity.*—Hitherto we have limited our attention to cases in which electricity is excited by the friction of dissimilar substances, and it may here be remarked that Peclet by a careful series of experiments found that the quantity of electricity developed was the same whether *sliding* friction was employed, as in the ordinary mode of exciting the electrical machine, or whether it was a *rolling* friction, in which the rubber was pressed against the cylinder and allowed to roll upon its axis as the machine was worked. The development of electricity by friction is, however, but a special case of a much more general law, for it has been found that, whenever molecular equilibrium is disturbed, a concomitant development of electricity takes place. The following instances will exhibit the variety of circumstances under which this observation has been made. The mere compression of many crystallized bodies is attended by electric action: a rhombohedron of Iceland spar, if compressed by the fingers, exhibits this peculiarity. It is also found that all bodies that have been pressed together, if properly insulated, offer signs of electricity on being separated; although the effect is most easily observed between a good conductor and a bad one. The two bodies are always in opposite states. Even where two disks of the same substance are pressed together, if one be a little warmer than the other, distinct excitement is produced, the warmer disk becoming nega-

tively electrified; the charge, *cæteris paribus*, increases in all cases directly as the pressure to which they are subjected.

Fracture is likewise attended with electric disturbance; the freshly broken surfaces of roll sulphur often exhibit this effect to an extent sufficient to produce divergence of the leaves of the electroscope when the fragments are placed upon the cap of the instrument. The sudden rending asunder of the laminæ of a film of mica in a dark room, is usually attended with a pale electrical light, and the separated portions in this case exhibit opposite electrical states. A melted substance in the act of solidifying, sometimes exhibits electric excitement. If sulphur be allowed to solidify in a glass vessel, it becomes negatively excited, whilst the glass is rendered positively electrical; ice also is frequently electric; and the same thing has been observed of chocolate as it becomes solid. These results are probably due to friction occasioned by the contraction or expansion of the solid mass in the mould, from which it detaches itself by this change of bulk.

In some instances simple elevation or depression of temperature causes electric excitement. These effects are most distinctly seen in crystallized non-conductors which are not symmetrical in form, being produced in bodies which are hemihedral. Tourmaline, boracite, and the crystals of tartaric acid, offer the best examples of this description. The tourmaline, for instance, commonly assumes the form of a three-sided prism, the edges of which are replaced by two narrow planes. The extremities of the crystal are formed by the three faces of the rhombohedron. No. 1, fig. 200, shows the end of the crystal which becomes positive by heat; No. 2, the opposite end of the crystal which becomes negative. If a crystal of tourmaline be gently heated, it becomes powerfully electrical whilst the temperature is rising, one extremity, termed the *analogous* pole, becoming positive, the other extremity, or *antilogous* pole, becoming negative.* When the temperature becomes stationary, the electric excitement ceases: as the crystal

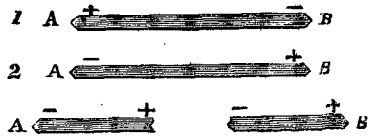
FIG. 200.



* The crystal must not be too strongly heated,—about 302° (150° C.) being the best point; if heated very strongly, 752° (400° C.) or beyond, the tourmaline becomes a conductor for a time: it resumes its insulating power on cooling, but is rendered hygroscopic till after it has been washed and dried at 302° (150° C.)—Gaugain.

cools the effect returns, but the electric polarity is reversed; the end of the crystal that before was positive now becomes negative. The particles of the mineral are electrically polarized throughout the whole mass; for if the crystal be broken while thus electrified, each fragment retains its polarity, being negative at one end and positive at the other. In fig. 201, No. 1 represents a tourmaline in which the temperature is rising uniformly; No. 2 the same tourmaline in which the temperature is falling uniformly; and No. 3 shows the effect upon a cooling tourmaline which has been broken across. If the tourmaline be delicately poised upon its centre whilst cooling, these electric states may be rendered apparent by bringing an excited glass tube near to the mineral: one extremity will be attracted by the excited glass tube, while the other extremity will be repelled. If one end of the crystal be connected with the cap of a sensitive gold-leaf electroscope, whilst the other extremity is in conducting communication with the earth, the gold-leaves will diverge.

FIG. 201.



(246) *Chemical Action.*—No chemical changes take place without the development of electricity. If a clean platinum capsule be connected with a sensitive electroscope and condenser, and a liquid which has no chemical action on platinum be placed in the capsule, no change shows itself; but if any other more oxidizable metal in conducting connexion with the earth be dipped into the liquid, the *liquid becomes very feebly but positively electrified, whilst the metal which has been acted upon by it becomes negative.* The intensity of the chemical action in this form of the experiment has no influence upon the extent of electric excitement displayed. If zinc be the metal employed, and pure water the liquid, the signs of electric action are just as powerful as if sulphuric acid were substituted for the water in the capsule; for the metal and liquid being both good conductors, the two electricities liberated, immediately neutralize each other almost entirely, instead of passing one to the condenser, the other to the earth.

Electricity is also developed during the process of combustion; carbon, for example, becoming negatively electric, whilst the carbonic anhydride is positive. In like manner hydrogen in the act of burning was found by Pouillet to be negative, whilst the vapour produced by it was positive.

(247) *Electricity of Vapour.*—The act of evaporation has also

been asserted to be one of the sources of electricity, but the truth of this statement is doubtful. It is true that if a few drops of water fall upon a live coal, insulated on the cap of the gold-leaf electroscope, the leaves of the instrument diverge. This, however, is due to the chemical action between the coke and the water, and not to mere evaporation; for if we allow pure water to evaporate in a clean hot platinum dish connected with the electroscope, no signs of electric disturbance occur. Pouillet found that on allowing alkaline solutions to evaporate in the capsule, the electroscope became charged positively; with acid solutions, the charge given to the electroscope was negative; but Peltier states that these electrical effects may nevertheless be due to friction, as they do not manifest themselves until the liquid is nearly all driven off, and a crepitation of the salt as it detaches itself from the sides of the capsule begins to occur. This is corroborated by Faraday's observation, that if the dish be heated to redness, and pure water be dropped in, so long as it evaporates quietly in the spheroidal form (198) no electricity is developed; but the moment that it cools down sufficiently to boil violently with friction against the metallic capsule, the leaves diverge powerfully.

In accordance with this observation, Faraday has explained the development of electricity by high-pressure steam, which occurs to so remarkable an extent under certain circumstances. This he has traced to the friction of water accompanying the steam against the orifice of the jet through which it escapes into the air. An insulated boiler from which steam is allowed to blow off at high pressure through long tubes, in which a partial condensation of the steam occurs, furnishes, as in the *hydro-electric machine* of Armstrong, exhibited a few years ago at the Polytechnic Institution, an admirable source of high electric power. In this experiment, the boiler becomes negative, the escaping steam being positive. It is remarkable that the presence of a very small quantity of oil or of essence of turpentine in the exit-pipe reverses these electrical states. A solution of plumbic acetate produces a similar effect. Indeed the purer the water that is used in the boiler, the better it is for these experiments, and the more uniform are the results. The electric condition of the steam was found by Armstrong to be also influenced by the material of which the exit-pipe was formed; glass, lead, copper, and tin, each modifying the result. Wood appears to be the material best adapted for use in forming the orifice of the jet, as it produces the highest amount of charge by friction; some bodies, such as ivory, produce scarcely any electric effect when used as jets to the pipe.

Perfectly dry steam is in fact nearly as good an insulator of electricity as atmospheric air; but, from the facility of its condensation, it easily produces upon cold surfaces a film of conducting matter which destroys the insulation.

(248) *Atmospheric Electricity.*—Another source of electricity, the origin of which is at present shrouded in mystery, is the atmosphere itself, which affords displays of electric phenomena on the most magnificent scale. The identity of lightning and electricity had long been suspected by electricians; but the proof of it was first devised by Franklin, who by the simplest expedient of raising a boy's kite during a thunderstorm, succeeded in obtaining from the clouds, sparks of electricity, with which he charged Leyden jars and performed some of the usual electrical experiments. Such kite-flying, however, forms a dangerous kind of recreation; and experiments on atmospheric electricity proved fatal to Professor Richman of St. Petersburg, who, a few years after Franklin's discovery, was killed by a flash from his apparatus.

No sooner had Franklin proved the identity of lightning with electricity, than he proposed his plan of averting the destructive influence of lightning from buildings, by means of metallic conducting-rods. In order to render these efficient, they must project into the air for some distance beyond the highest point of the building to be protected. They must also be sufficiently thick to carry off the discharge without fusion. This is insured by the use of a copper rod of not less than $13^{mm.}$ or half an inch in diameter. The pieces composing these rods should be in metallic contact with each other throughout their length, and the conductor should terminate in a bed of moist earth, or better still, in a well or body of water, so as to secure free communication with the soil. If any considerable metallic mass, such as a leaden roof, form part of the building; it should be connected with the conductor by branch rods, and should also be furnished with branch conductors into the earth. The conductors are best placed exterior to the walls of the building.

The explosive power of lightning is so great that its effects may well excite our awe and amazement. A single instance may be cited in illustration of this point. In November, 1790, the mainmast of H.M. ship *Elephant*, 74 guns, was struck by a powerful flash of lightning. This mast weighed 18 tons, it was 3 feet (0·914 metres) in diameter, and 110 feet (33·5 metres) long, and was strongly bound together by iron hoops, some of which were half an inch ($12·5^{mm.}$) thick and 5 inches (12·7 centimetres) wide; yet it was shivered into pieces, and the hoops were burst open

and scattered around, amidst the shattered fragments of the mast (Harris). One of the most instructive instances recorded is that of the *Dido*, which when off Java Head, in May, 1847, was struck soon after daylight, during a storm attended with heavy rain and little wind, by a tremendous bifurcated flash of lightning, which fell upon the main royal mast. One of the branches struck the extreme point of the royal yard-arm, and in its course to the conductor on the mast, demolished the yard, and tore in pieces or scorched up the greater part of the sail; the other part fell on the vane-spindle (the point of which showed marks of fusion) and truck, which last was split open on the instant that the discharge seized the conductor. From this point, however, the explosive action ceased, and the discharge freely traversed the whole line of the conductor from the mast-head downward, without doing further damage. One of the chief points of interest connected with this case is the entire destruction of the yard-arm, which was not supplied with a conductor, and the complete protection of the mast, which was furnished with one. It is also important as proving the incorrectness of the law of protection laid down by some French writers—viz., that a conducting-rod will protect a circular area having a radius double the height of the conductor above the highest point of the building. In all cases, the lightning will take the path of least resistance, and, from the recorded results of experience, it appears that that path of least resistance will in about seven times out of ten, be such that the lightning will strike the highest point, if it be furnished with a good conducting line to the earth or sea; but it is quite possible that instances may occur, in which the line of least resistance may be in a different direction, or, as in the case of the *Dido*, that there may be two such lines where the resistances are equal.

If a break occur in any part of the conductor, explosion will take place at this spot when a discharge of lightning is directed upon the rod, producing, in many cases, fearful destruction. One of the most awful catastrophes of this kind occurred on the 18th of August, 1769, when the tower of St. Nazaire of Brescia was struck by lightning. Beneath this tower were vaults containing upwards of 90 tons of gunpowder, belonging to the Republic of Venice. The whole of this enormous quantity of powder exploded, destroying one-sixth part of the city of Brescia, and burying 3000 persons beneath its ruins. On a small scale the track followed by the electricity may be illustrated by sending a discharge through a series of interrupted conductors, such as gold-leaf pasted upon paper. The portions of gold-leaf in the

line of the discharge will be burned up, whilst the contiguous portions not included in the track of the electricity remain unaltered.

The peal of thunder which accompanies the lightning flash is due, like the snap which accompanies the discharge of a Leyden jar, to the sudden displacement of air, which, in the case of lightning, sometimes extends through a distance of a mile or more. The reverberation of the peal arises chiefly from the echoes produced by objects upon the earth, and by the clouds themselves. The flash from the thunder-cloud is exactly analogous to the discharge of the Leyden jar: the cloud and the surface of the earth form the two coatings to the intervening layer of air, which, as in the case of the condenser, supplies the place of the glass, whilst a church steeple, or any projecting object, acts the part of a discharging rod.*

But it is not only during a storm that the atmosphere exhibits signs of electricity. In a cloudless sky, if a flame or a pointed rod be connected with an electroscope, the instrument diverges positively. Before rain, the instrument often assumes a negative state: in general, the rain that first falls after a depression of the barometer is charged negatively. It frequently happens that the rain is negatively charged, although the atmosphere, both before and after its fall, exhibits signs of positive charge. Fogs, snow, and hail, if unattended with rain, are nearly always positively charged in a high degree. It appears to be probable that the clouds are almost always positive. In most cases, when negative electricity is observed in the instruments it is simply due to an effect of induction.

Palmieri has conducted observations on atmospheric electricity for twenty-five years in the observatory on the side of Mount Vesuvius, and has obtained some results which point to a definite law. If within a distance of about 50 miles there is no shower of rain, hail, or snow, the electricity of the air is always positive, except during the projection of ashes from the volcano. During a shower the electricity is positive, surrounded by a zone of negative, and beyond this the air is again positive. Whenever the air is negative, therefore, it indicates that there is a heavier shower not far off. If the storm is approaching the

* These electrical accumulations are often renewed with extraordinary rapidity. On the 6th of July, 1845, about 10 P.M., after a clear hot day, in the masses of vapour forming a bank of cumuli, I counted in two minutes 83 flashes unattended by thunder; and several times during the same evening, I observed between 30 and 40 discharges from one cloud to another, per minute.

observatory, the air becomes negatively charged, then positively when the storm is near, negatively again after it has passed over, and again positively when the shower has moved to a considerable distance (*Nature*, 1872, vi. 146). These results explain the frequent variations during storms which are often observed in other localities, although it must be noticed that meteorological phenomena in Italy take place with much greater regularity than in this country.

In winter, the atmospheric charge is usually higher than in summer. According to Quetelet, whose conclusions are based upon a series of five years' uninterrupted observations, the atmospheric electricity attains an average maximum in January, and steadily decreases till June, when it is at its minimum: from this period it again increases progressively till January, in which month the tension of the electricity is thirteen times as high as it is in June. The electricity of the air may be stated generally to be higher in a cloudless than in a cloudy sky. Only once during the months of October, November, December, and January, has he obtained proof of negative electricity in the air.

The tension of the charge varies likewise during each twenty-four hours; it has two maxima and two minima. The first maximum is before eight o'clock A.M. in summer, and before ten A.M. in winter; the second after nine P.M. in summer, and before six P.M. in winter. The first minimum is uniformly about four A.M., and the second about three P.M. in summer, and one P.M. in winter.

The observations made for some years at the Kew observatory by Ronalds, furnish results closely according with those of Quetelet.*

An ingenious experiment by Becquerel shows that the intensity of the charge increases with the elevation above the earth's surface, and according to Quetelet's observations, the increase in intensity is proportional to the height. This law of Quetelet has, however, been verified only for heights not exceeding 16 feet (5 metres). Becquerel's experiment was the following:—Having ascended Mount St. Bernard, he placed an electroscope upon a piece of varnished silk, on which he arranged by a loose cord about 80 metres of gilt thread. One end of this thread he attached to the shaft of an arrow, and connected the other ex-

* For an interesting discussion of the theory of the development of atmospheric electricity, the reader is referred to Delarive's *Traité de l'Electricité*, iii. 188 *et seq.*

tremity with the cap of an electroscope by a running knot. The arrow was then discharged in a vertical direction by means of a bow; as it ascended the leaves expanded gradually till they struck the sides of the glass. When the full length of the thread was attained, the upward motion of the arrow detached it altogether from the electroscope, leaving the instrument charged positively. On repeating the experiment, shooting the arrow horizontally, no charge at all was obtained. Similar results may be obtained on a clear day by ascending a lofty eminence or building, to avoid the induction of near objects, and taking a gold-leaf electroscope, terminating above in a ball. The electroscope being now in a neutral state, it will, if elevated only for a foot or two, diverge with positive electricity. On bringing it back to its original position, the leaves collapse, and on depressing it below this point, the leaves again separate with the opposite electricity.

Two methods for collecting atmospheric electricity have been devised by Sir William Thomson. When a pointed conductor is raised in the air, a charge is induced upon it which is opposite to that contained in the atmosphere. If the atmospheric charge is considerable, there will be, as in the lightning conductor, a discharge from the point; but when the charge is very feeble, no such discharge may take place. If, however, the conductor loses some of its matter from the point, the induced charge will be carried off, and the other end of the conductor will exhibit the same kind of electricity, and of the same potential, as that contained by the air surrounding the point. This loss of matter may be effected by the burning of a slow match, made by soaking a roll of filter paper in a solution of plumbic nitrate, or by employing a fine jet of water, breaking into drops at the point in the air at which it is desired to measure the charge. By means of the water-dropping collector connected with a quadrant electrometer, a continuous photographic record of atmospheric electricity is made at the Kew observatory.

Electricity develops itself in the atmosphere in other forms; for example, luminous brushes, stars, and glows, have been frequently observed in stormy weather on the extremities of the masts and yard-arms of ships, on the points of weapons, and occasionally even on the tips of the fingers. These phenomena are, in fact, cases of brush discharge upon a large scale, and are in many instances attended with a roaring noise like that of a burning portfire. Appearances of this description formerly went by the name of *St. Elmo's fire;* our own sailors term them *comazants.*

(249) *Aurora Borealis.*—Another very beautiful meteor which is sometimes seen in this country in clear frosty nights, but which is observed very frequently in higher latitudes, has probably an electrical origin. This is the *aurora borealis.* It has been supposed to be occasioned by the passage of electricity through the rarefied portions of the upper regions of the atmosphere from the poles towards the equator, but the explanation is unsatisfactory, and not adequate to account for the effects observed. The varieties of coloured light exhibited by the aurora may, however, be imperfectly imitated on a small scale by discharging a continued or an intermittent supply of electricity through a vessel partially exhausted of air.

The forms which the aurora assumes are very varied, and of extraordinary beauty; there is, however, usually some general similarity in its aspect at the same locality. Commonly, streams of light are seen shooting upwards from the northern horizon. These streams are frequently observed to meet together in the zenith, and produce an appearance as if a vast tent were expanded in the heavens, glittering with gold, rubies, and sapphires.

A remarkable connexion has been observed between the aurora and the magnetism of the earth; the magnetic needle being very generally disturbed during a display of the aurora. The arches of the aurora most commonly traverse the sky at right angles to the magnetic meridian, though deviations from this direction are not rare. Sir J. Franklin found that the disturbance of the needle was not always proportionate to the agitation of the aurora, but was always greater when the quick motion and vivid light were observed to take place in a hazy atmosphere. The aurora is most frequent and vivid in high latitudes towards either pole; but the meteor is not confined to these parts, as Dr. Hooker states that one of the most brilliant displays he ever witnessed was under the tropical sky of India; and other observers have recorded instances of its appearance in the equatorial districts of the globe.

The altitude of the aurora varies considerably; there is no doubt, however, that it frequently occurs at small elevations. Both Franklin and Parry record examples of its appearing below the level of the clouds, which they describe as concealed behind the masses of its light, and as reappearing when the meteor vanished. There appear to be two distinct kinds of aurora, one dependent upon local causes, as in the cases last mentioned, while, in the other, the causes are probably cosmical, and the

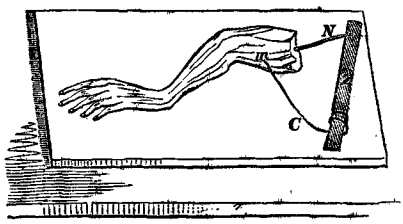
auroral effects are seen at very distant points of the earth's surface. (Sabine.)

The occurrence of the aurora is closely associated with sun-spots, magnetic storms, and earth-currents; there is also a period of maximum and minimum frequency, which is identical with that of the sun-spots, namely, 11·11 years.

§ III. Galvanic or Voltaic Electricity.

(250) *Galvani's Discovery.*—About the year 1790 Galvani made the observation that convulsive movements were produced in the limbs of a frog recently killed, if brought into contact with two dissimilar metals, such as zinc and copper, which were themselves in contact. The experiment may be readily repeated in the following manner:—Expose the crural nerve (N, fig. 202) of a recently killed frog, touch it with a strip of zinc, z, and at the same time touch the surface of the thigh, *m*, with one end of a bit of copper wire, c; the moment that the other end of the copper wire is made to touch the zinc, the limb is convulsed: but the convulsions cease when the two metals are separated from each other, though they are still in contact with the animal tissues. Each time that the zinc and copper are made to touch each other, the convulsion is renewed. A live flounder laid upon a pewter plate shows no particular sign of uneasiness; a silver spoon may also be laid upon its back without any apparent effect; but if the spoon be made to touch the pewter while it rests on the fish, the animal becomes strongly convulsed. If a piece of zinc and a shilling be placed one above and the other under the tongue, no particular sensation is perceived so long as the two metals are kept separate, but if the silver and the zinc be allowed to touch each other, a peculiar tingling sensation or taste is experienced; and if the silver be placed between the upper lip and the teeth instead of under the tongue, each time that the two metals are brought into contact, not only will a taste be perceived, but a momentary flash of light will appear to pass before the eye.

Fig. 202.

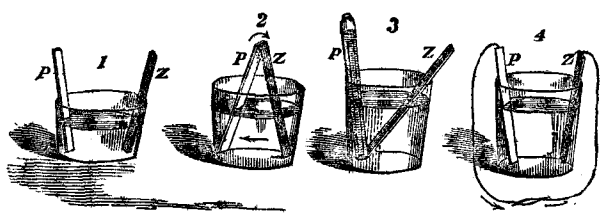


These phenomena are all analogous to each other, and have an electrical origin: and by tracing them to this source, a branch

of electrical science has gradually been developed, which in honour of its first discoverer has been termed *galvanism*. The term galvanism, or *voltaic electricity*, as it is also called, in remembrance of the researches of Volta in this field, is applied to electricity which is set in motion by chemical action. It is usually developed by the contact of two dissimilar metals with a liquid.

(251) *Elementary Voltaic Circuits.*—These effects may be traced by very simple means. When a plate of zinc is immersed in diluted sulphuric acid, an evolution of hydrogen gas takes place from the surface of the metal, and the zinc becomes dissolved in the sulphuric acid. But if the surface of the zinc, after it has been cleansed by immersion in the acid, be rubbed over with mercury, a brilliant amalgam is speedily formed over the whole face of the zinc. Such a plate may then be plunged into the acid, and it will remain without undergoing any chemical change for hours. The cause of this inactivity of the zinc is not satisfactorily accounted for, but the fact is continually made use of in voltaic experiments. The addition of a second amalgamated zinc plate, whether it be in contact with the first or be separated from it, produces no change. But if the second plate be of platinum, of copper, or of some metal which is less rapidly acted on by the acid than zinc is, although no action will occur whilst the two plates remain separate (as shown in fig. 203, 1), yet the

FIG. 203.



moment that they are allowed to touch each other, either above (2) or beneath (3) the surface of the liquid, bubbles of gas will escape from the surface of the platinum. The platinum, however, is not acted upon chemically in this case; if the two metals be weighed before the experiment is commenced, and again after it is concluded, the weight of the platinum will be found to be unaltered; but the zinc will have been partially dissolved, and will weigh less than it did before. The gas may easily be collected by filling a tube with diluted acid, and, after introducing the platinum plate, inverting the tube in the glass, so that the

lower edge of the platinum may touch the strip of zinc (No. 3). On examining the gas which rises in the tube it will be found to be pure hydrogen. It is not necessary that the two plates should directly touch each other. They may be connected by means of a metallic wire (as at 4, fig. 203), by a piece of graphite, or by any good conductor of electricity: gas will continue under these circumstances to rise from the platinum plate; but if a glass rod, a stick of shell-lac, a bit of gutta-percha, or any electric insulator be made the medium of intercommunication, all signs of action will cease. The length of the metallic wire employed is comparatively unimportant: it may vary from a few centimetres to many miles, and in either case it will enable the action across the liquid to take place. A pair of plates of dissimilar metals in effectual communication, either by direct contact or through the medium of wire, when immersed in a liquid which acts chemically upon one of them, constitutes a *voltaic circuit.*

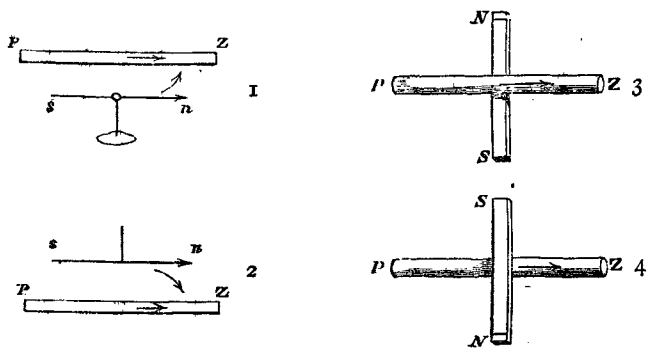
(252) *Activity of the Conducting Wire.*—The wire or other medium of communication, during the time that it forms the connexion between the two metals, exhibits signs of activity which it did not before possess; it exerts a variety of influences upon surrounding bodies, and it loses these powers immediately that the contact with the metallic plates is broken. For instance, the temperature of the wire is for the time elevated. This may be proved by causing the wire to traverse the bulb of a sensitive air thermometer, or by making a compound metallic ribbon, such as is used in Breguet's thermometer (140), part of the chain of communication between the plates. If a portion of the wire be sufficiently reduced in thickness, visible ignition of such portion may even be produced. Indeed the quantity of heat given out by the connecting wire may be employed as a measure of the amount of electricity which it is transmitting.

(253) *Action of the Conducting Wire on the Magnetic Needle.*—Another remarkable proof of the activity of the wire which connects the two metallic plates, is exhibited in the peculiar influence which it exerts over a magnetic needle suspended freely at its centre in a direction parallel to the wire (Œrsted, *Ann. Chim. Phys.* 1820 [2], 417). Such a needle tends to place itself at right angles to the wire. If the wire and the needle be previously arranged in the magnetic meridian, the deviation in the needle affords a comparative measure of the electricity which is conveyed by the wire, as the needle ultimately assumes a position of equilibrium between the directive power of the earth's magnetism and that of the wire (301).

The movements of such a magnetic needle afford one of the most delicate tests of the development of galvanic electricity, or of electricity in motion. It will therefore be necessary to examine the direction and nature of these movements.

The direction of the needle under any circumstances may easily be calculated by recollecting the following rule:—*When the wire is placed in the magnetic meridian, with the end connected with the zinc plate towards the north, and the needle is placed below the wire, the marked end will deviate westward.* When the needle is above the wire, the marked end will move towards the east. The first effect is shown in fig. 204, 1; the second in 2. On reversing

FIG. 204.



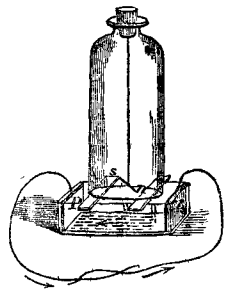
the attachment of the wire to the plates, the phenomena will in each case be inverted. By means of a simple model, the direction of the needle under any conditions may be readily indicated:—Across a square strip of wood nail a cylindrical piece at right angles; let the square rod represent the magnetic needle, the round rod the connecting wire (fig. 204, 3 and 4), then mark upon the square rod the letters N and S, and on the round rod, P and Z, in conformity with the rule just given: by placing the model in any given position, the relative effect of the wire upon the needle under these circumstances will be shown.

Another simple method by which the position of a magnet acted on by a current may be remembered is the following:—Place the palm of the right hand towards the magnet, and when the current is passing in a direction parallel to the hand and towards the ends of the fingers, the thumb will point to the north-seeking end of the magnet.

Even the liquid part of a voltaic circuit acts thus upon the magnetic needle. This may be shown by suspending a needle, *n s*, fig. 205, by means of a fibre of silk, over a dish of diluted sulphuric acid. On one side of this dish a zinc plate, z,

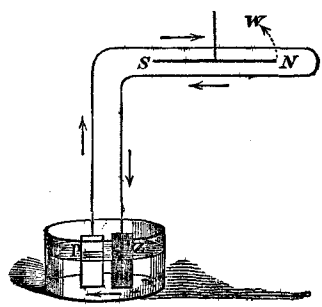
is inserted, on the other, a plate of platinum, P. The needle must be placed so that one of its ends may point towards one plate, and the other end towards the other plate. If the two plates be now connected by a wire, as shown in the figure, the needle will be deflected, and will place itself nearly parallel to the metallic plates.

Fig. 205.



(254) *The Galvanometer.* — Since every part of the circuit acts equally upon the needle, and since it is possible to make several parts act simultaneously upon it, actions may be rendered perceptible which would otherwise be too weak to influence its motion. Fig. 206 will convey an idea of the principle upon which this is effected. Suppose the wire connecting the plates P and Z to be bent into a loop with parallel sides. If a magnetic needle be suspended between the wires, and parallel to them, the loop and the needle being both in the magnetic meridian, with the end N pointing to the north, the marked end of the needle would be impelled westward under the influence of the force in the upper branch; and as the current returns in the reverse direction through the lower wire, this tendency of the north end westward would be doubled. By increasing the number of coils which are placed around the needle parallel to each other, very feeble actions may be rendered evident. An instrument constructed on this principle is termed a *galvanometer* or *rheometer* (or 'current measurer,' from ῥέω, to flow).

Fig. 206.

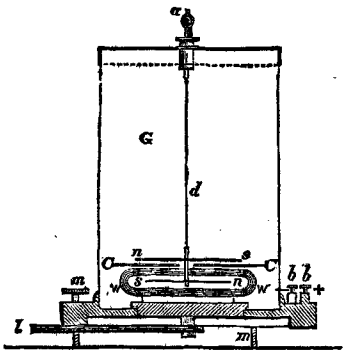


The sensitiveness of the galvanometer may, however, be still further increased by placing outside the coil a second magnetic needle with its poles reversed; the directive force of the earth may be thus almost exactly neutralized; its attraction upon the north end of one needle being almost exactly counterbalanced by its repulsion upon the south end of the needle which is parallel to it. A pair of needles thus arranged constitutes what is termed an *astatic* combination (from ἄστατος, unstable). A very feeble current will be sufficient to drive one particular extremity of such a pair of needles to the east or to the west; but the second needle being outside the coil, will be acted upon by the upper wires only, the lower ones being at too great a distance to produce any sensible

effect. The action of the upper wires upon the needle above them coincides with their action upon the lower needle, with its reversed poles: and the effect of a feeble current is thus materially increased by these combined actions. The conducting wire must be covered with silk with a view to preserve each coil duly insulated from the contiguous ones.

The *astatic galvanometer* is represented in fig. 207. The needles, *n s*, *s n*, are suspended, one within and the other above the coil of wire, *w w*, by means of a fibre of silk, *d*, the whole being enclosed within the glass case, G. The parallelism of the two needles to each other is maintained under all circumstances by causing each of them to pass transversely through the same piece of straw, or by connecting them together by means of a piece of fine copper wire; the fibre *d* is attached to the upper extremity of the straw or the wire. By means of a screw at *a*, the point of suspension of the silk can be raised or lowered without twisting it, so that when the needles are not in use their weight need not be supported by the silk fibre. c c, is a sheet of copper provided with a graduation on its margin for estimating the angular deviation of the needles; *b*, *b*, are binding screws for connecting the extremities of the coil with the wires which transmit the current;* the apparatus can be levelled by means of the screws. *m m*; and at *l*, a lever is shown by which the coil of wire, *w*, can be placed accurately parallel with the magnetic needles, so as to make them coincide with the zero of the graduated circle. Such an instrument may be made not only to indicate the existence of voltaic action, but also to measure its amount. When the deviations of the needle are small, not exceeding 15° or 20°, the number of degrees of deviation gives nearly accurately the relative force; but for angles of greater

Fig. 207.

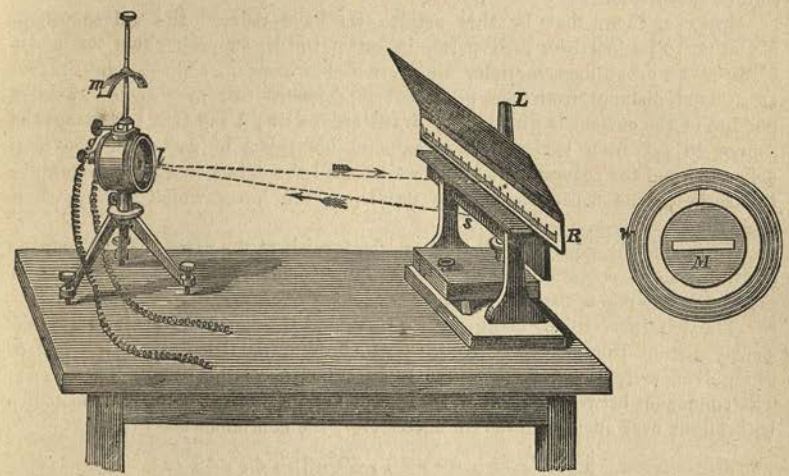


* Instead of binding-screws, it is not uncommon to employ small cups containing mercury as the means of completing the metallic communication between the different parts of the circuit; the ends of the wires should be made perfectly bright before immersing them in the mercury. Copper wires may be easily amalgamated superficially by scouring them with fine emery-paper and moistening them with a solution of mercuric nitrate; the perfection of the contact is thus insured.

magnitude, this is not the case, because the more the needle deviates from parallelism to the wire, the more obliquely and therefore the less powerfully does the attraction or repulsion act which occasions its motion; and it becomes necessary to determine the value of the degrees by direct experiment. It would require a greater current to move the needle from 20° to 25°, than from 10° to 15°: and a still greater to produce a deviation from 30° to 35°; but the current required in each case is definite, and consequently may be estimated and measured.*

Thomson's Reflecting Galvanometer.—This is a very sensitive and beautiful instrument, which is now used extensively for telegraphic purposes. The indi-

FIG. 208.



cating magnet is attached to the back of a small circular silvered mirror, shown separately at M, fig. 208, the joint weight of the two not exceeding 1·5 grain

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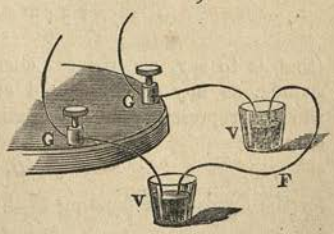
* Melloni's method of graduating a galvanometer is the following, quoted by Tyndall (*Heat considered as a Mode of Motion*, 4th edit. 330):—Two small vessels, V, V, fig. 209, are half filled with mercury, and connected separately by two short wires, with the extremities, G, G, of the galvanometer. The vessels and wire thus disposed make no change in the action of the instrument, the thermo-electric current being freely transmitted as before from the pile to the galvanometer. But if, by means of a wire, F, a communication be established between the two vessels, part of the current will pass through this wire and return to the pile. The quantity of electricity

FIG. 209.



(0·1 grm.). The mirror and magnet are suspended by a few fibres of unspun silk, in the centre of a helix of insulated wire, *w*; in the central opening of the coil is placed a small lens; the coil is supported in a suitable frame, *g*, mounted on levelling screws. Upon a perpendicular rod fastened to the top of this frame a magnet, *m*, slides up and down, so as to enable the operator by its means to neutralize the effect of the earth's magnetism upon the needle of the galvanometer. In front of the instrument a lamp, L, is placed behind a vertical slit, *s*, which is arranged at a suitable distance from the galvanometer, in a line of the prolongation of the axis of the coil at *g*. The light of the lamp passes through the slit, *s*, and is concentrated by the lens upon the mirror, from which it is reflected through the lens upon the scale R; this scale being placed at a distance suited to the production upon its graduated surface of a sharp reflected image of the slit. Since a very slight angular deviation of the needle causes the spot of light to traverse

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circulating in the galvanometer will be thus diminished, and with it the deflection of the needle.

Suppose, then, that by this artifice we have reduced the galvanometric deviation to its fourth or fifth part—in other words, supposing that the needle being at 10 or 12 degrees under the action of a constant source of heat placed at a fixed distance from the pile, that it descends to 2 or 3 degrees when a portion of the current is diverted by the external wire; I say that by causing the source to act from various distances, and observing in each case the total deflection and the reduced deflection, we have all the data necessary to determine the ratio of the deflections of the needle, to the forces which produce these deflections.

To render the exposition clearer, and to furnish at the same time an example of the mode of operation, I will take the number relating to the application of the method to one of my thermo-multipliers.

The external circuit being interrupted, and the source of heat being sufficiently distant from the pile, to give a deflection not exceeding 5 degrees of the galvanometer, let the wire be placed from V to V; the needle falls to 1°·5. The connexion between the two vessels being again interrupted, let the source be brought near enough to obtain successively the deflections:—

$$5°,\ 10°,\ 15°,\ 20°,\ 25°,\ 30°,\ 35°,\ 40°,\ 45°.$$

Interposing after each the same wire between V and V, we obtain the following numbers:—

$$1°{\cdot}5,\ 3°,\ 4°{\cdot}5,\ 6°{\cdot}3,\ 8°{\cdot}4,\ 11°{\cdot}2,\ 15°{\cdot}3,\ 22°{\cdot}4,\ 29°{\cdot}7.$$

Assuming the force necessary to cause the needle to describe each of the first degrees of the galvanometer to be equal to unity, we have the number 5 as the expression of the force corresponding to the first observation. The other forces are easily obtained by the proportions:—

$$1{\cdot}5 : 5 = a : x = \frac{5}{1{\cdot}5}a = 3{\cdot}333\ a$$

(that is to say, one reduced current is to the total current to which it corresponds, as any other reduced current is to its corresponding total current), where *a* represents the deflection when the exterior circuit is closed. We thus obtain—

$$5,\ 10,\ 15{\cdot}2,\ 21,\ 28,\ 37{\cdot}3,$$

for the forces corresponding to the deflections—

$$5°,\ 10°,\ 15°,\ 20°,\ 25°,\ 30°.$$

In this instrument, therefore, the forces are sensibly proportional to the arcs,

the entire length of the scale, the equidistant graduations may be taken as exactly proportional to the power of the current. By dividing the helix into coils of different lengths, which portions may be used independently, and by shifting the position of the magnet many degrees of sensitiveness may be obtained with the same instrument, rendering it applicable to a large number of experiments, in which the quantity of the current varies within wide limits.

(255) Allusion has already been made to the physiological action of the current, in consequence of which, if a living animal, or a part of one recently killed, such as the limb of a frog, be included between a pair of plates, muscular contractions are produced; similar effects occur if a portion of the human body, such

---

up to nearly 15 degrees. Beyond this the proportionality ceases, and the divergence augments as the arcs increase in size.

The forces belonging to the intermediate degrees are obtained with great ease either by calculation or by graphical construction, which latter is sufficiently accurate for these determinations. By these means we find—

Degrees ...	13°	14°	15°	16°	17°	18°	19°	20°	21°
Forces ...	13	14·1	15·2	16·3	17·4	18·6	19·8	21	22·3
Differences		1·1	1·1	1·1	1·1	1·2	1·2	1·2	1·3
Degrees ...	22°	23°	24°	25°	26°	27°	28°	29°	30°
Forces ...	23·5	24·9	26·4	28	29·7	31·5	33·4	35·3	37·3
Differences		1·4	1·5	1·6	1·7	1·8	1·9	1·9	2

In this table we do not take into account any of the degrees preceding the 13th, because the force corresponding to each of them possesses the same value as the deflection.

The forces corresponding to the first 30 degrees being known, nothing is easier than to determine the values of the forces corresponding to 35, 40, 45 degrees, and upwards.

The reduced deflections of these three arcs are—

$$15°{\cdot}3,\ 22°{\cdot}4,\ 29°{\cdot}7.$$

Let us consider them separately, commencing with the first. In the first place, then, 15 degrees, according to our calculation, are equal to 15·2; we obtain the value of the decimal 0·3 by multiplying this fraction by the difference 1·1, which exists between the 15th and 16th degrees; for we have evidently the proportion—

$$1 : 1{\cdot}1 = 0{\cdot}3 : x = 0{\cdot}3.$$

The value of the reduced deflection corresponding to the 35th degree will not therefore be $15°{\cdot}3$, but $15°{\cdot}2 + 0°{\cdot}3 = 15°{\cdot}5$. By similar considerations we find $23°{\cdot}5 + 0{\cdot}6 = 24°{\cdot}1$ instead of $22°{\cdot}4$, and $36°{\cdot}7$ instead of $29°{\cdot}7$ for the reduced deflections of 40 and 45 degrees.

It now only remains to calculate the forces belonging to these three deflections—$15°{\cdot}5$, $24°{\cdot}1$, and $36°{\cdot}7$—by means of the expression $3{\cdot}333\ a$; this gives us—

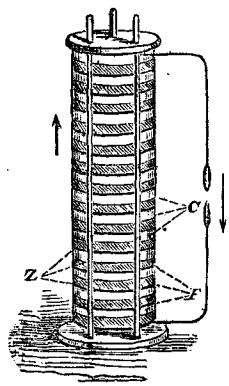
The forces	51·7	80·3	122·3
For the degrees ...	35°	40°	45°

Comparing these numbers with those of the preceding table, we see that the sensitiveness of our galvanometer diminishes considerably when we use deflections greater than 30 degrees.

as the tip of the tongue, be included between two interrupted points of the conducting wire. But in addition to the heating, magnetic, and physiological effects, another remarkable series of phenomena, those of chemical decomposition, may be exhibited at the interrupted points of the conducting wire. These, however, are more distinctly shown when a number of pairs of plates is employed.

(256) *The Voltaic Pile.*—In prosecuting the experiments of Galvani, Volta discovered that by using a number of similar metallic pairs moistened by a saline or by a feebly acid liquid, many of the effects already described were greatly increased; and in the year 1800 he published a description of the apparatus which he had contrived, and which has perpetuated the name of its inventor under the designation of the *Voltaic Pile.* This important instrument is represented in fig. 210.

FIG. 210.

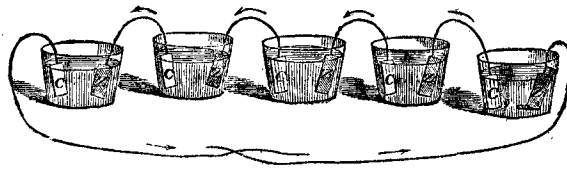


It consists of a succession of pairs of plates of two dissimilar metals, such as zinc, z, and copper, c, or zinc and silver, each pair being separated on either side from the adjacent pairs by pieces of card or of flannel, F, moistened with salt and water, or with very weak acid: these plates may be supported by a frame of dry wood. The effects produced by such an apparatus were soon seen to be of an electrical character. If the ends of the pile or the wires connected with them were touched, one with each hand previously moistened, a sensation similar to that of the electric shock was experienced. Sparks could be obtained between two pieces of charcoal attached to the ends of the wires; divergence of the gold leaves of the electroscope was produced when one wire touched the cap of the instrument, whilst the other wire was in communication with the earth; and other electrical effects were obtained. In arranging the plates of metal it is necessary strictly to observe a certain order in their succession; thus, if a plate of zinc with a wire attached to it form the bottom of the pile, a piece of wet flannel must be placed upon it, then a piece of copper, then a piece of zinc, then flannel, then copper, then zinc, then flannel, and so on, till the pile terminates at the top with a plate of copper to which a wire is attached. By soldering together the zinc and copper in pairs, a considerable improvement is effected; complete contact of the two metals is insured, and the apparatus can be mounted with more rapidity. Many practical inconveniences, however,

are experienced when the instrument is mounted in the form of a pile: the liquid in the flannel soon loses the power of acting chemically on the zinc, and the activity of the combination declines rapidly.

Another more effectual arrangement adopted by Volta is shown in fig. 211; he termed it the *Crown of Cups*. In this form, the liquid in the cell corresponds to the moist flannel of the pile, and

FIG. 211.



the zinc of one cell being connected with the copper of the *adjacent* cell, the arrangement corresponds exactly with that of the pile, where the zinc is on one side of the flannel, whilst the copper in contact with the other surface of the flannel communicates with the zinc touching the flannel next above it, and so on. Other more efficient forms of the voltaic battery will be described further on.

The Conditions required to produce Voltaic Action.

(257) *Electric Disturbance by Contact of Dissimilar Metals.*—Having in the foregoing remarks traced the voltaic phenomena to a modification of electricity, we may now proceed to examine more particularly the conditions under which they occur.

It was early observed by Volta that when two different metals, properly insulated, are brought into contact, and then separated by means of insulating handles, each plate exhibits signs of electricity which may be detected by a sensitive electroscope such as Bohnenberger's (*note*, § 298). The more oxidizable metal is found to be positive, while the less oxidizable metal is negative. If zinc filings be sifted through a piece of insulated copper-wire gauze upon the cap of a gold-leaf electroscope, the leaves of the instrument will diverge. On approaching the electroscope with an excited stick of sealing-wax the leaves will collapse, thus proving that the zinc filings have acquired positive electricity. If copper filings be sifted through zinc gauze, the filings will be found to be negative. The various metals may, with reference to these electric actions, be arranged in a series in which those first in order become positive by contact with all those that follow, and

negative with all those that precede: for example, potassium, zinc, iron, lead, tin, copper, mercury, silver, gold, platinum. This, it may be observed, is merely the order of the oxidizability of the different metals, and Delarive contends with great probability that the development of electricity in Volta's experiment is due to an excessively minute oxidation produced by the moisture of the air upon the plate which becomes positive, although the experiments by which he attempts to prove the point are not absolutely conclusive.

It was originally maintained by Wollaston that the electricity developed in the ordinary machine when an amalgam is used for exciting the action of the rubber, was produced mainly by the chemical act of oxidation exerted by the atmosphere upon the metal. But this view is shaken by the experiments of Peclet, who excited his electrical machine in a vessel filled successively with dry carbonic anhydride and dry hydrogen, and he found that in these gases as much electricity was evolved as when the same machine was surrounded, *cæteris paribus*, by dry air. Talc and plumbago may also be used with good effect upon the rubber as substitutes for the amalgam, though no effect of oxidation can be supposed to occur when these bodies are employed.

Volta regarded the interposed liquid of his pile in the light merely of an imperfect conductor which allowed induction to take place through it, the electrical equilibrium being perpetually disturbed by the contact of the two metals; and he overlooked the chemical changes which the liquid is constantly undergoing.

Sir William Thomson has devised an experiment for showing the charge produced on two metals by their simple contact. A light aluminium needle is supported near one end by a metallic wire connected to a Leyden jar, a counterpoise being placed on the short end of the needle so that it may rest in a horizontal position. If a disc of metal is placed beneath the needle and the Leyden jar charged positively or negatively, the needle will show no tendency to be deflected either to the left or to the right; if the disc be now replaced by two half discs of different metals, such as zinc and copper, so situated that their line of junction is vertically under the needle, then a deflection is observed when the needle is charged. If charged positively the needle will be attracted by the half disc of copper and be repelled by the zinc, showing that the zinc has become positively and the copper negatively charged. If the half discs be slightly separated and connected together by a metallic wire, the same result is obtained, but if instead of a metallic wire a drop of water be

placed between the half discs no deflection of the needle is observed. (*Electrostatics and Magnetism*, by Sir W. Thomson, p. 317. See also Fleming Jenkin's *Electricity and Magnetism*, 2nd Edit., 1874, 45.)

(258) *Chemical Action essential to the Production of Voltaic Action.*—It is now known that chemical changes are essential to the production of the force. Contact of dissimilar substances, it is true, is necessary to the voltaic action; because without contact there can be no chemical action. Such contact produces disturbance of the electric equilibrium in the bodies which are brought together, and thus occasions a state of tension or polarity which always precedes the discharge. Chemical action, by renewing these contacts and by furnishing appropriate conductors to the electricity thus accumulated, maintains the action and accurately measures its amount; and until chemical action occurs no current is produced. The following experiment may be cited in illustration of this point:—Let an iron wire be connected with one extremity of a galvanometer of moderate sensibility, and a platinum wire with the other extremity; immerse the ends of the wires in highly concentrated nitric acid (sp. gr. about 1·45), without allowing them to touch each other in the liquid; no chemical action will occur upon the iron, and no movement of the magnetic needle will be produced; but the addition of a little water will determine a rapid solution of the iron in the acid, and the needle will receive a powerful impulse at the same moment that the chemical action commences.

(259) *Polarization and Transfer of the Elements of the Liquid.*—The simple occurrence of brisk chemical action is not alone sufficient to produce a powerful voltaic effort. The metals are all excellent conductors of electricity, and, in combining with each other to form alloys, they often give evidence of intense chemical action, but they do not produce any adequate voltaic effect. For example, if a small quantity of tin be placed in a tube bent into the form of the letter U, and be melted by the heat of a spirit-lamp, and it be connected on one side with the wire of a galvanometer, which is introduced into the melted metal in one limb of the tube, whilst into the second limb of the tube a platinum wire, connected with the other extremity of the galvanometer, is plunged, the platinum will unite with the tin with incandescence, but after the first moment of contact but a slight deviation of the magnetic needle will be observed, although a brisk chemical action is continued for several seconds. A solution of the elementary bodies, chlorine or bromine, when used as the liquid between the plates,

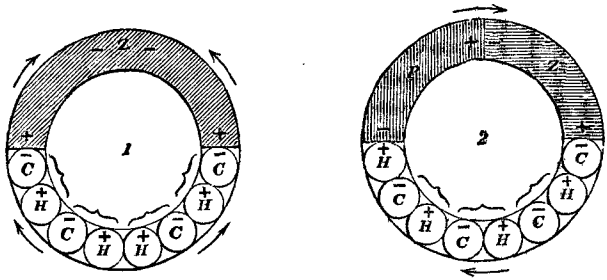
although it acts powerfully on the zinc, produces by no means a proportionate effect in the circuit.

In order that the liquid shall possess any marked power of exciting voltaic action, it must be a compound susceptible of decomposition by one of the metals, such, for instance, as dilute sulphuric, hydrochloric, or hydriodic acid, or a saline substance, such as sodic chloride or potassic iodide. This necessity for the employment of a compound liquid for exciting the force, appears to arise from the necessity of a peculiar polarization in the liquid in order to enable it to transmit the voltaic action. Indeed, in all voltaic actions the transfer of power is effected by a polar influence, propagated through both the solid and the liquid particles of the circuit, and the chain of conducting material must be continuous throughout, so that the force shall *circulate*.

This process of polarization may be conceived to occur in the following manner, which offers an explanation of the mode in which the platinum (or the plate of metal which corresponds to platinum) may be supposed to act:—When a plate of pure zinc or of amalgamated zinc is immersed in a compound liquid, which, like a solution of hydrochloric acid (HCl), is capable of attacking it chemically, the metal at the points of contact becomes positively electrified, whilst the distant portion becomes negative. The layer of liquid in contact with the zinc undergoes polarization, which affects each molecule of its chemical constituents; the particles of chlorine (C) become negative, and the particles of hydrogen (H) positive: but in this form of the experiment there is no communication between the distant negative part of the zinc and the positively electrified particles of hydrogen; consequently, beyond the production of this state of electric tension, no change ensues. This condition is represented in fig. 212 (1). But the case is entirely altered if a plate of platinum, or of some other metal which is not easily acted upon by the acid, be introduced, and made to touch the zinc. By contact with the zinc the platinum itself becomes polarized; it imparts a certain amount of positive electricity to the zinc, and receives a portion of negative in return, and transmits the polar action to the liquid. A chain of polarized particles is thus produced, as represented in fig. 212 (2); the chlorine of the particle of HCl nearest the zinc becomes negative under the influence of the chemical attraction which exists between it and the zinc, and the hydrogen becomes positive: the second and third particles of HCl become similarly electrified by

induction; but the platinum, under the influence of the induction of the zinc, being negative, is in a condition to take up the positive electricity of the contiguous hydrogen. The action now rises

FIG. 212.



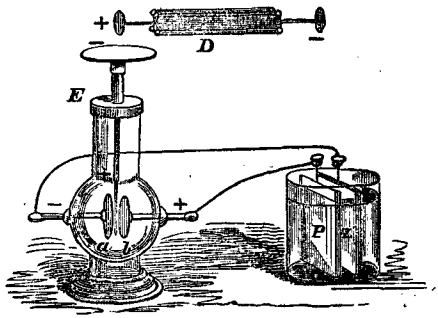
high enough to enable the zinc and the chlorine to combine chemically with each other: the zincic chloride thus produced is dissolved by the liquid, and is removed from further immediate action; but the particle of hydrogen nearest the zinc now seizes the oppositely electrified chlorine which lies next to it, and a new portion of hydrochloric acid is reproduced, whilst the hydrogen in the second particle of the acid is transferred to the chlorine of the adjacent particle, and the particle of hydrogen which terminates the row is electrically neutralized by its action upon the platinum, to which it imparts its excess of positive electricity, and immediately escapes in the form of gas. Fresh particles of hydrochloric acid continually supply the place of those which have undergone decomposition, and in this way a continuous action is maintained. Thus the transfer of electricity from particle to particle of the liquid is attended at the same instant by a transfer of the constituents of the liquid in opposite directions.

These changes are not successive, but are simultaneous in each cross section of the liquid, and are also attended with corresponding changes at all points of the entire circuit. These changes when continued uninterruptedly constitute what is conveniently termed a *voltaic current*. This term, 'current,' is in general use, but it should be borne in mind that it is in this sense employed merely to signify the continuous transmission of electrical action, not of any material substance. In every voltaic current it is assumed that a quantity of negative electricity, equal in amount to that of the positive set in motion, is proceeding along the wire in a direction opposed to that in which the positive electricity is travelling; and it is conceived that by the perpetual separation

and recombination of the two electricities in the wire, its heating and other effects are produced. In order to avoid confusion, however, whenever the *direction* of the voltaic current is referred to, the direction of the positive current alone is indicated.

The polarization of the metallic and liquid particles composing a circuit when zinc is placed in an acid, or, in other words, the occurrence of electric tension as a preliminary to the passage of the voltaic current, may be shown by the following experiment (Gassiot). A plate of platinum, P, fig. 213, and another of amalgamated zinc, Z, are immersed in dilute sulphuric acid, and the wire which proceeds from each is insulated and connected with the two gilt disks, *a*, *b*, of the electroscope, E; these disks are insulated from each other and from the ground by the glass of the apparatus; they slide easily to and fro in the sockets, and can be brought within a quarter of an inch ($6^{min.}$), or less of each other; a single gold leaf, mounted as in the ordinary electroscope, is suspended midway between them: now if the positive end of a Deluc's pile (298), D, be brought near the cap of the instrument, the gold leaf will approach the disk, *a*, which is connected with the zinc plate; the leaf becomes positive by induction from the positive end of the pile, and is therefore attracted by the negatively electrified disk, *a*, but if the opposite end of the pile, D, which is charged with negative electricity, be presented, the gold leaf becomes negative, and is attracted by the positively electrified disk, *b*, which is in connexion with the platinum plate. The amount of the electric tension increases in proportion as the number of pairs is increased. Gassiot found with a battery of 400 pairs of Grove's cells, each cell being carefully insulated, that a succession of sparks passed between the terminals when brought very near to each other; and if each end of the battery was connected with a gold-leaf electroscope, the leaves of each electroscope diverged powerfully, the wire in connexion with the platinum plate furnishing positive, that with the zinc plate, negative electricity. (299.) The tension of the electricity at the poles of even one cell of a voltaic battery may be measured by means of Thomson's electrometer. (226.)

FIG. 213.



(260) *Energy of the Current proportionate to the Chemical Activity.*—In order to produce a current, the two metals which are employed must be acted upon by the exciting liquid with different degrees of rapidity:—when, for instance, two similar slips of zinc, or of any other metal, are opposed to each other, no current is excited. The galvanic action is strongest between two metals upon which the chemical action of the components of the exciting liquid differs most widely: for, from what has been already stated, it is evident that two strips of zinc would tend to produce polarization, and subsequently currents of equal intensity in op-

posite directions, so that the two would necessarily neutralize each other. When zinc is opposed to tin, a current is produced setting out through the liquid from the zinc to the tin; zinc and copper give rise to a stronger current in the same direction; whilst between zinc and platinum the current is still more powerful; and between potassium and platinum the action attains its maximum. By forming an amalgam of potassium, this last-mentioned experiment admits of easy performance; for it has been found that the voltaic relations of all amalgams are the same as those of the more oxidizable metal which they contain. A good deal of the potassium is oxidized by what is termed *local* action, without contributing in any way to the production of the current. The distinction between local action and action which contributes to the voltaic effect is important, and may be illustrated by the difference in action of diluted sulphuric acid upon a slip of ordinary zinc and upon a slip of zinc from the same sheet which has been amalgamated: in the first case rapid solution of the metal will occur although the connexion with the platinum plate may remain incomplete; in the second, the zinc will be attacked only when the circuit is completed; but the unamalgamated zinc will produce no greater voltaic effect than an equal slip of the metal which has been properly amalgamated. In no instance is the electricity in circulation increased or diminished by the local action on the plates, whatever be the nature of the metal, the employment of amalgamated zinc plates merely economising zinc and acid.

Wheatstone has devised a method (274) of measuring the amount of the *electro-motive force*, or energy of the voltaic power produced by any combination; and he has by this means proved conclusively that this energy depends upon the intensity of the chemical action between the elements of the liquid and the metals which compose the circuit. He has shown that if any three of these dissimilar metals be taken in their electrical order and be formed in pairs into separate circuits, the force generated by a combination of the two extreme metals of the series is equal to the sum of the forces developed when the intermediate metal is separately combined with each of the other two in succession. For example, the voltaic energy, or electro-motive force excited between platinum and an amalgam of potassium may be represented by the number 69: the electro-motive force between platinum and zinc, expressed in terms of a similar standard, is equal to 40; and in a similar experiment between zinc and potassium,

where zinc acted the part of a negative metal towards the potassium, the number obtained was 29. Now

the electro-motive force between platinum and zinc = 40
the electro-motive force between zinc and potassium = 29

the two taken together = 69

and this number, 69, is identical with that obtained by opposing platinum to the amalgam of potassium.

(261) *Direction of the Current dependent on the Direction of the Chemical Action.*—In all these cases the positive electricity sets out from the more oxidizable metal, which may be termed the positive, or generating plate, and traverses the liquid towards the less oxidizable metal which forms the negative or conducting plate: from the conducting plate the force is transferred to the wire, and thence in turn to the generating plate; and in this way the circuit is completed. Unless this circulation can take place all the phenomena of voltaic action are suspended. Since the chemical action of any combination is thus always in one uniform direction, the motion of a magnetic needle under its influence is equally uniform; the current which is produced, whether it be measured by its magnetic or by its heating effects, is proportioned to the quantity of the positive metal which is dissolved in a given time.

Every liquid which is active in exciting a voltaic current may be regarded as consisting of two groups of substances, one of which attacks the generating or positive plate, and may be termed the electro-negative constituent of the liquid, whilst the other is transferred to the conducting or negative plate, and constitutes the electro-positive constituent.

The elementary bodies have indeed been classified upon this principle into electro-positive and electro-negative substances; hydrogen and most of the metals being electro-positive; oxygen, chlorine, and other substances of this nature being electro-negative. In the following table the more important of the elements are arranged in their electro-chemical order on the authority of Berzelius. It has been remarked that the more strongly electro-positive metals crystallize in forms belonging to the regular system, whilst the non-metallic elements, and those metals which are most electro-negative, crystallize generally in other forms.

Electro-chemical Order of the Principal Elements.

Electro-negative.	
Oxygen	Gold
Sulphur	Platinum
Selenium	Palladium
Nitrogen	Mercury
Fluorine	Silver
Chlorine	Copper
Bromine	Bismuth
Iodine	Tin
Phosphorus	Lead
Arsenic	Cadmium
Chromium	Cobalt
Vanadium	Nickel
Molybdenum	Iron
Tungsten	Zinc
Boron	Manganese
Carbon	Uranium
Antimony	Aluminium
Tellurium	Magnesium
Titanium	Calcium
Silicon	Strontium
Hydrogen	Barium
	Lithium
	Sodium
	Potassium
	Electro-positive.

It is probable that the order here followed is not exactly correct. Fluorine, and chlorine, perhaps, ought to stand at the head of the list; there is no doubt that hydrogen should stand much nearer to potassium; and according to late experiments aluminium should take its place between lead and cadmium. It is also certain that the elements do not under all circumstances maintain the same relative order, but that in particular cases the order is altered: for example, in strong nitric acid iron is nearly as electro-negative as platinum; again, a metal may be electro-positive when it forms the basyl of a salt, but electro-negative when associated with the elements of the acid constituent. Indeed it may be laid down as an invariable rule that whenever the chemical action is inverted the direction of the current is inverted also. The voltaic order of the metals given above is that which is observed when diluted acids are used as the exciting liquids,

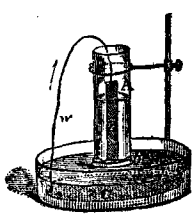
but it by no means represents the order in which they stand when the current is excited by the use of a caustic alkaline solution or a sulphide of the alkaline metals. This point is well exemplified in the following results given by Faraday (*Phil. Trans.*, 1840, 113). The metals which stand first on each list are negative to all those which follow them. The place of iron in the strong nitric acid is that which it shows immediately on immersion; it becomes much more powerfully electro-negative afterwards:—

Dilute Sulphuric Acid.	Dilute Nitric Acid.	Dilute Hydrochloric Acid.	Nitric Acid Sp. Gr. 1·48.	Solution of Caustic Potash.	Yellow Sulphide of Potassium.
Silver	Silver	Antimony	Nickel	Silver	Iron
Copper	Copper	Silver	Silver	Nickel	Nickel
Antimony	Antimony	Nickel	Antimony	Copper	Bismuth
Bismuth	Bismuth	Bismuth	Copper	Iron	Antimony
Nickel	Nickel	Copper	Bismuth	Bismuth	Lead
Iron	Iron	Iron	Iron	Lead	Silver
Lead	Tin	Lead	Tin	Antimony	Tin
Tin	Lead	Tin	Lead	Cadmium	Cadmium
Cadmium	Cadmium	Cadmium	Zinc	Tin	Copper
Zinc	Zinc	Zinc	Cadmium	Zinc	Zinc

The relative size of the generating and conducting plates has no influence upon the direction of the current, which sets in as certainly through the liquid from a square centimetre of zinc to a square metre of copper as from a square metre of zinc to a square centimetre of copper. The spread of this action may be traced in an interesting manner by substituting a solution of cupric sulphate for sulphuric acid as a part of the exciting liquid; copper will be thrown down instead of hydrogen, and by its colour and thickness will very accurately indicate the extent and direction of the action.

The experiment is easily made by taking advantage of a property possessed by porous diaphragms, in consequence of which, a piece of any animal membrane, or of unglazed earthenware, which can be thoroughly wetted by the liquids, will allow the current to traverse it without opposing any material obstruction to its passage. Diluted sulphuric acid may thus be employed upon one side of the diaphragm, and a solution of cupric sulphate upon the other side: under these circumstances a current would be freely transmitted, whilst the two liquids would be prevented from intermingling. For example, let a piece of bladder, *b*, fig. 214, be tied firmly over the lower end of a wide tube open at both extremities; place some diluted sulphuric acid, A, in the tube, and suspend a rod of amalgamated zinc, z, in its axis; support the tube so that its lower end shall dip beneath the surface of a solution of cupric sulphate, s, contained in a

FIG. 214.



shallow glass dish, upon the bottom of which rests a sheet of copper, C: on connecting the zinc and copper by the wire, *w*, voltaic action will ensue, and a deposit of metallic copper will be produced upon the plate, C. It will, however, be observed that this deposit does not take place uniformly over the surface of the sheet, C, but that it commences in the centre in a circular form; the layer of copper shows itself first at the point immediately beneath the extremity of the zinc rod, and it is at this point that the greatest thickness of the deposit occurs; it gradually becomes thinner towards the circumference of the circle, which, however, continues to increase in diameter as the experiment proceeds, until, if sufficient time be allowed, the plate is covered with reduced copper.

Whilst a metal is thus rendered electro-negative by voltaic action, it is no longer liable to the ordinary action of chemical agents. A beautiful application of this principle was made by Davy to the prevention of the corrosion of the copper sheathing of ships by the action of sea water. Copper is the material best adapted to preserve the timbers of the ship from the attacks of marine insects and boring animals; but this metal, when subjected, under ordinary circumstances, to the combined influence of the salts dissolved in sea water and of the atmospheric air which it also holds in solution, experiences corrosion, which in the course of a few years renders it necessary to renew the copper. It was, however, discovered by Davy, that by placing pieces of zinc, or of cast-iron, in contact with the copper under water, this corrosion could be prevented; and that a surface of zinc, not exceeding $\frac{1}{150}$ of that exposed by the copper, was adequate to the entire protection of the copper,—the whole of the chemical action being transferred to the zinc; and that even when the surface of zinc was reduced until it was only equal to $\frac{1}{1000}$ of that of the copper, a considerable preservative effect was experienced. But the very success of the experiment in the direction anticipated, created difficulties of another kind; earthy matters, consisting of compounds of calcium and magnesium, were deposited from the sea water by the slow voltaic action, and they attached themselves to the surface of the copper; weeds and shell-fish found in this deposit a congenial pabulum, the bottom of the ship became foul, the sailing qualities of the vessel were necessarily impaired, and the system of voltaic protectors was abandoned without sufficient trial under different modifications. For some years past a kind of brass, introduced by Mr. Muntz, which admits of being rolled whilst hot, has, in the merchant service, been largely and advantageously substituted for copper as a material for ships' sheathing. In this case the zinc and the copper are combined in the sheet itself, which is less rapidly corroded than if composed of either metal separately. The protective influence of zinc both on copper and on iron is readily shown by exposing

bright bars of these metals in separate vessels, either in sea water or in a solution of common salt containing 1 part of salt to 20 parts of water. If a fragment of zinc be attached to one of the bars of copper and to one of the bars of iron, these bars will remain bright, whilst the zinc is corroded; but the unprotected bars will, in a few hours, give evidence of the commencement of chemical action.

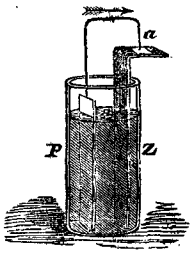
Another remarkable proof of the dependence of the current, for its direction and its intensity, upon chemical action, is afforded by the manner in which a voltaic circuit may be produced between two surfaces, one of which has a stronger attraction for *hydrogen* than the other possesses. For example, when two clean plates of platinum are immersed in diluted acid, and connected with a galvanometer, no voltaic action is excited; but the case is different if one of these plates be first coated with a film of some metallic peroxide, such as manganic dioxide (MnO_2), plumbic dioxide (PbO_2), or argentic peroxide (Ag_2O_2). The platinum plate may be thus coated by immersing it in a solution of manganous sulphate, of plumbic nitrate, or of argentic nitrate, and connecting it with the platinum side of a weak voltaic arrangement for a few minutes, whilst the liquid is connected by a second plate with the zinc end of the battery: the plate, after it has been thus coated with the peroxide, must be well washed with distilled water. If it be then opposed to a plate of clean platinum and immersed in any diluted acid, it will originate a current which depends upon the chemical attraction of the hydrogen of the diluted acid for the second atom of oxygen in the peroxide. In a combination of this description the clean platinum becomes positive, and corresponds to the zinc plate, whilst the coated platinum becomes negative. The coated plate, although negative, thus becomes the generating or acting surface, and transmits the current at once to the conducting wire.

Faraday has shown that the direct contact of dissimilar metals is not necessary to the production of the voltaic current, provided that they are connected by some liquid of sufficient conducting power. This is a point of considerable importance, for it shows that Volta's theory of the origin of the electro-motive force, which is still maintained by some philosophers who have not made the chemical phenomena of the pile their especial study, is incorrect.

The following is the simple experiment which proves the point now under discussion: z, fig. 215, is a plate of zinc, bent at a right angle; p, a platinum plate, to which a platinum wire is attached. At *a*, a small piece of blotting-paper, moistened with a solution of starch and potassic iodide, is interposed

between the plate of zinc by which it is supported and the platinum wire which rests upon it; no change occurs in the solution of the iodide until the two plates are immersed in diluted nitric acid; but in a few minutes after such immersion, evidence of a current in the direction of the arrow is afforded, by the appearance of a blue spot against the platinum wire, due to the liberation of iodine, from the decomposition of the potassic iodide by the voltaic action.

FIG. 215.

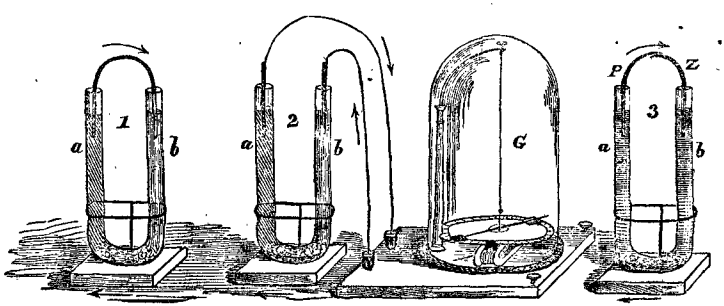


Fleming (*Proc. Phys. Soc.* 1874, i. 1) has constructed a battery in which no contact of dissimilar metals is permitted. The cells contain alternately dilute nitric acid and solution of sodic pentasulphide, and are connected alternately by plates of lead and copper. In the cells containing nitric acid the current passes from the lead through the liquid to the copper, and in those filled with sodic persulphide it flows from the copper through the liquid to the lead. If the terminals consist of copper, the wire may be wound round a galvanometer needle, when the existence of a current will be indicated.

(262) *Circuits with one Metal and two Liquids.*—For the establishment of a voltaic current, it is further necessary that the body which decomposes the liquid be a conductor of electricity, in order to carry off the force generated; but it is not necessary to use two dissimilar metals, provided that one extremity of the metal be plunged into a liquid capable of acting on it, whilst the other extremity dips into a different liquid which has little or no action on the metal, but which communicates freely with the first liquid.

Take, for example, a tube bent into the form represented in fig. 216, 1. Place a plug of tow in the bend; into one limb, *a*, pour a solution of cupric

FIG. 216.



chloride ($CuCl_2$), in the other limb, *b*, place a solution of common salt (NaCl) sodic chloride. Connect the open ends of the tube by bending a strip of copper so that one end of it shall dip into the solution of copper and the other end into the solution of salt. Crystals of copper will be formed gradually upon the end of the strip which is immersed in the metallic solution, whilst the end of the strip which is immersed in the salt and water will be slowly corroded, and cupric chloride will be formed. The following diagram may assist in explaining this change:—

A

(1.) Cu | $\overbrace{CuCl_2 CuCl_2}$ | $\overbrace{Na_2Cl_2 Na_2Cl_2}$ | Cu

(2.) CuCu | $\overbrace{Cl_2Cu, Cl_2}$ | $\overbrace{Na_2Cl_2 Na_2Cl_2 Cu}$ |

Let the symbol Cu Cl_2, represent the composition of cupric chloride, Na_2Cl_2 that of sodic chloride, the line at A being used to show the position of the plug of tow. If No. 1 indicate the state of things before any change has occurred, No. 2 will represent the change after the circuit is complete.

If the strip of copper be divided in the middle, and the two ends be connected with a galvanometer, G, as shown in fig. 216, 2, a current is found to be circulating through the apparatus. A still simpler arrangement may be adopted; if a long straight tube be filled half full with diluted sulphuric acid, and the remainder with a solution of cupric sulphate, a strip of copper plunged into it will be dissolved below, while an equal amount of copper will be deposited on the upper extremity; from the extreme slowness and regularity of the action, the deposited metal will assume the form of crystals. Becquerel, by using various liquids in the two limbs of the bent tube (No. 1) has obtained many of the metals crystallized in forms of great beauty.

By employing two dissimilar metals in the metallic arc, as P Z, (fig. 216, 3) a more powerful but equally regular action may be excited. If a solution of common salt be placed in one limb, *b*, and a solution of ferrous chloride in the other, *a*, whilst the zinc end of a compound arc of zinc and platinum is plunged into the first, and the strip of platinum is immersed in the second liquid, tetrahedral crystals of iron will in a few days be deposited upon the platinum. If a little zirconic chloride be mixed with the ferrous chloride in the limb *a*, plates of zirconium will be obtained, of a steel-grey colour, and which, by exposure to the air, become oxidized and fall to a white powder.

Becquerel has shown that within the strata of the earth similar actions are going on; and R. W. Fox and others, by connecting the surfaces of two contiguous lodes of metallic ore by means of wires attached to a galvanometer, have succeeded in demonstrating to the eye the existence of those feeble but continuous currents, which are probably the cause of the accumulation of the different metals in regular beds, and of their beautiful crystalline arrangement.

Other combinations may be produced, in which the mutual action of the two liquids originates the current, the metal merely serving as a conductor. Becquerel was the first to point out the means of obtaining circuits of this description, of which the following is a good example:—If a small porous vessel be filled with nitric acid, and be immersed in a second vessel containing a solution of caustic potash, on plunging two platinum plates connected with the wires of a galvanometer, one into the acid, the other into the alkaline liquid, a steady current of considerable intensity will be produced, and will be maintained for many days, in a direction passing from the potash to the nitric acid, and thence returning through the galvanometer to the alkaline liquid. A still more powerful combination was obtained by Matteucci on

substituting a solution of di-potassic pentasulphide for the caustic potash. A single cell of this construction decomposed acidulated water if interposed between the platinum wires, and on breaking contact a distinct spark was perceptible at the surface of the mercury employed to connect the two platinum wires. Arrott (*Phil. Mag.* 1843 [3], xxii. 427) has described a variety of other cases of this kind. These actions, however, will be more conveniently studied in connexion with the chemical effects of the voltaic battery, at a future point (289).

(263) *Summary.*—The conditions necessary to the production of a voltaic current may be shortly recapitulated as follows:—Though the contact of dissimilar metals produces electric disturbance, chemical action is necessary to propagate the voltaic current. This chemical action must be produced by means of a compound liquid, which is decomposed in the process, one of the constituents of the liquid entering into combination with one of the metals. In the transmission of the voltaic action a polarization of the liquid, as well as of the solid portions of the circuit, is produced, and this polarization of the liquid is attended with the separation of its constituents into two groups, one of which unites with the positive metal, whilst the other makes its appearance at the same moment upon the negative plate. The activity of the combination, or its electro-motive force is greater, the greater the difference between the chemical attraction of the electro-negative constituent of the exciting liquid for the two metals which are opposed to each other in the particular case. The relative size of the plates employed has no influence on the direction of the current which is produced. Contact of two metals is not necessary to the production of voltaic action: circuits may be formed between one metal and two liquids, if the liquids be in liquid communication with each other, and if their chemical attractions for the metal be unequal. If two dissimilar liquids exert a chemical action upon each other, it is even possible to obtain a current from their mutual action by connecting the liquids through the intervention of a metal upon which they exert no chemical influence, and which therefore simply performs the part of a conductor.

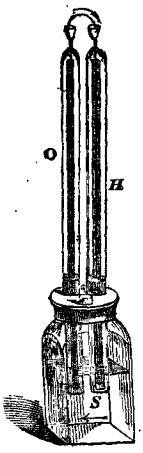
Different Forms of the Voltaic Battery.

(264) *Counteracting Currents: Gas Battery.*—We shall now resume the consideration of those forms of voltaic combination which are the most important in practice, and in which, generally, two dissimilar metals are employed.

It has been already stated that the amount of force set in motion in a voltaic arrangement depends upon the difference between the attraction of the two metals for the active principle or *radicle* of the acid. Under circumstances favourable to the production of a current, decomposition of the liquid which excites the action always occurs; the elements of the liquid are separated from each other, and they either combine with the metallic plate, or else they accumulate upon its surface, giving rise to the condition of the plates which is often described under the inappropriate term *polarization* of the plates or electrodes. These adhering substances oppose the voltaic action and enfeeble it, owing to the tendency of the separated components of the liquid to re-unite. When, for example, diluted sulphuric acid is used, it becomes a desideratum to get rid of the hydrogen which adheres to the platinum, and produces a current in the opposite direction. The existence of this counter-current may be rendered evident by connecting with one end of the wire of a galvanometer a platinum plate which has thus been opposed to a plate of zinc: on attaching to the other end of the galvanometer wire a second but clean platinum plate, and plunging both into diluted acid, a powerful deflection of the needle will be observed.

This observation has been ingeniously applied by Grove, who has constructed what he terms a *gas battery*, by opposing a plate covered with oxygen to the plate coated with hydrogen, whilst at the same time he increases the surfaces of contact between the platinum and the oxygen and hydrogen. Fig. 217 represents a cell of this battery. It consists of two tubes, O and H; through the upper extremity of each passes a platinum wire, which is fused into the glass, and attached to a platinum plate sufficiently long to reach to the bottom of the tube. The surfaces of these plates are coated by means of voltaic action with finely-divided platinum, for the purpose of increasing the surfaces of contact between the metal and the gas. The tube H has double the capacity of the tube O. These tubes are supported in the vessel, S, by the plug through which they pass. In order to use the apparatus, the vessel S is filled with diluted sulphuric acid, and by inverting the cell the tubes are likewise filled with the liquid. The plates in the tubes O and H are then connected by the mercury cups at top with the wires of a voltaic battery in action, so that by the decomposition of the diluted acid the tube O shall become filled with oxygen and the tube H with hydrogen. The tubes having been thus filled, the battery wires are withdrawn. If the mercury cups at the top of the tubes O and H be now connected with the wires of a galvanometer, powerful deflection of the needle will be produced, and a current will be maintained through the apparatus in the direction of the arrows. The two gases will gradually diminish in volume, and will in a few days

FIG. 217.



entirely disappear, but the current will be maintained so long as any portions of the gas remain uncombined. By connecting eight or ten such cells in succession, so that the oxygen tube of one cell shall be connected with the hydrogen tube of the adjacent cell, sparks may be obtained between charcoal points, and various chemical decompositions may be effected. The polar chain by which these changes are produced may thus be represented by symbols: H_2SO_4, indicating a molecule of diluted acid, O and H_2 representing the disturbing atoms of oxygen and hydrogen:—

$$\overbrace{O\,\underbrace{H_2\,SO_4}}\;\overbrace{\underbrace{H_2\,SO_4}}\;\overbrace{\underbrace{H_2\,SO_4}\,H_2}$$

The brackets above the row of symbols are intended to show the molecular arrangement before the circuit is completed; those beneath the symbols show the action during the passage of the current.

Since no action occurs in the gas battery until metallic communication between the plates is effected, it appears that the use of the platinum plates consists in favouring the action by condensing the gases upon their porous surfaces, and in acting as conductors of the current.

It may indeed be stated generally, that the accumulation of either of the elements of the exciting liquid upon the metallic plates of a voltaic combination, always tends to produce a counter-current, and therefore reduces the efficiency of the combination to a proportionate extent. Hydrogen is the element which, in the usual mode of experiment, principally accumulates upon the negative plate, so that any contrivance by which the adhering hydrogen is removed, exalts the energy of the circulating force. This removal of the hydrogen may be effected by means which act either on chemical or on mechanical principles. The chemical principle is the most perfect. It consists in adding to the liquid a compound which has a tendency to unite with the hydrogen; hence the energy of the current is much increased by mixing a little nitric acid (HNO_3) with the exciting liquid, comparatively little hydrogen being set free in this case.* The same end is attained by adding to the sulphuric acid a solution of some of the metallic salts, such, for instance, as cupric sulphate ($CuSO_4$). When cupric sulphate is employed, metallic copper is deposited upon the negative or conducting plate, whilst the sulphion with which it was previously united combines with the zinc. A disadvantage, however, is experienced when the liquid which absorbs the hydrogen is in contact with the zinc, and this is particularly evidenced when cupric sulphate is used. The zinc acts at once

* By the action of hydrogen on nitric acid, peroxide of nitrogen (N_2O_4) and water are formed, thus: $2HNO_3 + H_2 = N_2O_4 + 2H_2O$; and both these substances are dissolved by the nitric acid.

on the solution of copper, and becomes coated with reduced copper: hence, between the particles of zinc and those of the reduced copper innumerable small circuits are produced, which occasion a violent discharge of hydrogen from the entire surface of the generating metal, or rather from the copper deposited upon it; but the zinc thus dissolved contributes nothing to the general effect; it becomes merely a case of local action (260).

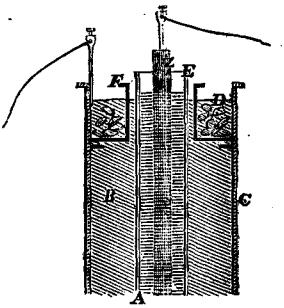
This experiment with the cupric sulphate throws light upon the cause of the effervescence which takes place when common zinc is treated with diluted sulphuric acid. Commercial zinc always contains lead and other foreign metals mixed with it in very appreciable quantity; these act as dischargers to the hydrogen, and give rise to numerous local circuits at all points of the surface of the zinc. Perfectly pure zinc is dissolved very slowly in acid for want of these discharging points, but the acid is not absolutely without action upon the metal. Any inequality in susceptibility to chemical action gives rise to a current between two substances suitably disposed; hence any difference in density between two pieces of the same metal may suffice to cause a current; and a piece of hammered zinc will generally act as a conducting plate to a piece of zinc well annealed. The adherence of a film of oxide or of fatty matter to the surface of one piece will also cause a difference, and hence two pieces of metal which may even have been cut from the same strip may, under certain circumstances, produce a feeble current.

The inconvenience which is occasioned by local action, when nitric acid or cupric sulphate is mixed with the liquid which is in contact with the zinc, may be avoided by the employment of porous diaphragms; and if the zinc or generating plate be plunged into diluted sulphuric acid, whilst the platinum or conducting plate is made to dip into the nitric acid or into the solution of cupric sulphate, which is separated from the generating plate by means of a tube of porous earthenware, combinations of great efficiency are obtained.

(265) *Daniell's Battery.*—These important facts were first clearly enunciated by Daniell. Their application to the voltaic battery enabled him to detect the cause of the rapid decline in the activity observed in all the forms of batteries which up to that period had been devised, and they led him to the invention of an arrangement which not only obviated these defects, and enabled him to keep up a current of constant strength for many hours, but also furnished electrical science with a battery of far greater activity for its size than any which had previously been used.

Fig. 218 exhibits a section of one of the cells of Daniell's combination. The outer case, C, consists of a cell, or cylinder of copper, which is constructed so as to retain liquids, and is filled with a solution of cupric sulphate, B, acidulated with an eighth of its volume of sulphuric acid. The solution is kept saturated with the salt by means of crystals of cupric sulphate, D, which rest upon the perforated shelf, F. In the axis of the cell is placed a tube of porous earthenware, E, filled with an acid solution, A, which consists of 1 part of oil of vitriol diluted with 7 parts of water. A rod of amalgamated zinc, Z, is placed in this tube. On making a metallic communication between the zinc rod and the copper cell, a voltaic current is established: and by employing twenty or thirty cells of this description, always connecting the zinc of one cell with the copper of the next, a combination of great power is obtained.

FIG. 218.



The following diagram may serve to explain the manner in which the force is transmitted through the cells:—The diluted sulphuric acid may be regarded as a compound of hydrogen with sulphur and oxygen, and is represented as H_2SO_4; whilst cupric sulphate may be looked upon as a compound of copper with the same compound of sulphur and oxygen, and is indicated by the formula $CuSO_4$. Let the brackets above the row of symbols represent the connexion of the particles which compose the liquid before contact is made between the plates Cu and Zn at the ends. The alteration in the molecular arrangement of the liquid which occurs after the connexion is made between the copper and the zinc, may be represented by the altered position of the brackets beneath: the line A, which divides the symbols of the cupric sulphate from those of the sulphuric acid, in this case represents the porous diaphragm:—

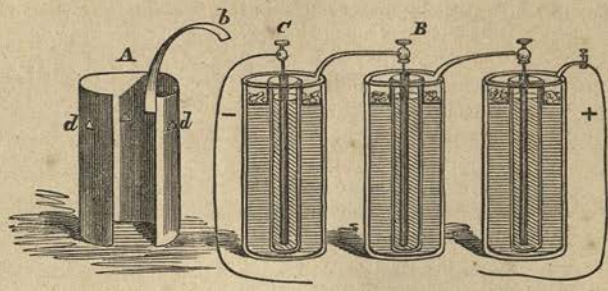
$$\underbrace{Cu}\ \overbrace{\underbrace{Cu\,SO_4}\ \underbrace{Cu\,SO_4}}^{A}\ \Big|\ \overbrace{\underbrace{H_2\,SO_4}\ \underbrace{H_2\,SO_4}}\ \underbrace{Zn}$$

The result of the action is, that so long as the contact between the metallic plates is maintained, zincic sulphate is formed uninterruptedly in the porous tube, whilst a continual deposit of a corresponding quantity of metallic copper takes place upon the internal surface of the copper cylinder.

Fig. 219 shows a convenient and inexpensive form of Daniell's battery. The solution of cupric sulphate is contained in glass or earthenware jars 7 inches (18 centimetres) high and $3\frac{1}{2}$ inches (9 centimetres) in diameter. The copper plates consist merely of rectangular sheets of copper, one of which is represented at A; they are bent in a cylindrical shape and placed in the jars. By means of the strip *b*, each plate is easily connected with the zinc rod of the adjacent cell, and made fast to it by the binding-screw C. The colander, for the support of the

crystals of cupric sulphate, rests upon three or four little pieces of copper, which are made to project inwards upon the sheet, at a suitable height, as shown at *d*. At B, several cells of the battery are represented as arranged

FIG. 219.

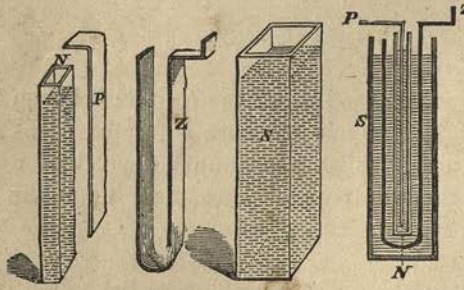


in a consecutive series. Twenty such cells compose a battery adequate to the performance of almost any experiments on the chemical decomposition of bodies in solution.

It is essential in mounting a voltaic arrangement of any kind, that the surfaces of contact between the metals be perfectly clean: a film of oxide will materially impede the transmission of the current, and if the force in circulation be feeble, it may even arrest it altogether. As a precaution, it is better before connecting the different parts of the apparatus, to pass a file or a piece of emery-paper over all the surfaces of the copper, the zinc, or the other oxidizable metals which are to be placed in contact with each other. Surfaces of platinum, if well washed and dried, do not need friction with emery-paper.

(266) *Grove's Nitric-Acid Battery.*—The nitric-acid battery, contrived by Grove, is a still more powerful combination on the same principle as Daniell's. It consists of a slip of platinum, P, fig. 220, which is plunged into the porous cell, N, and this is filled up with undiluted nitric acid. The outer cell, S, is filled with diluted sulphuric acid, and in this acid is placed a flat sheet of amalgamated zinc, Z, bent so as to infold the porous cell. The acid liquid in S may be conveniently made of 1 measure of oil of vitriol diluted with 4 measures of water. This combination presents in a small compass the principal desiderata for attaining

FIG. 220.



intense voltaic action. Platinum is the least liable of the metals to chemical action, whilst amongst the metals that admit of being easily wrought, zinc is the one which is most readily attacked by acids; consequently the opposition of platinum to zinc furnishes a most effective voltaic combination; whilst nitric acid absorbs with ease the hydrogen liberated on the platinum, and thus forms water and nitrous acid, which remain in solution in the undecomposed acid; the resulting liquid constitutes one of the most perfect of liquid conductors. If HNO_2O in the following diagram represent nitric acid, and H_2SO_4 diluted sulphuric acid, Pt the platinum plate, and Zn the zinc one, the molecular arrangement will be indicated before the action by the position of the brackets above, and after the action by the position of those below.

$$\underbrace{\overbrace{Pt\,H\,NO_2\,O}}\;|\;\underbrace{\overbrace{H_2SO_4}\,\overbrace{H_2SO_4}\,\overbrace{Zn}}$$

With a battery of ten such cells, 5 inches (12 centimetres) high and $2\frac{1}{2}$ inches (6 centimetres) wide, a large number of brilliant experiments may be performed, but four or five cells are generally sufficient for most purposes of electro-chemical decomposition. If oil of vitriol be mixed with the nitric acid in the porous cells in the proportion of about equal measures, a current is thus obtained, the strength of which is more uniform than when nitric acid only is used (Callan).

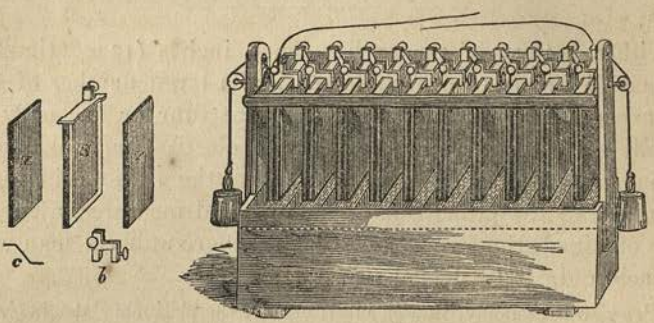
With a view to economy, Bunsen substitutes for the platinum plates in Grove's battery, cylinders of carbon, prepared by heating together a mixture of powdered coke and caking coal, or powdered coke moistened with a strong solution of sugar. A firm coherent cake is thus obtained. Cylinders made of this material answer well while new; but being porous, the carbon absorbs the nitric acid, which corrodes and impairs the surface of contact with the zinc. A better material is the hard carbon from the gas retorts, but it is difficult to shape it into the form of plates. Poggendorff has employed plates either of sheet iron or cast iron instead of either platinum or carbon; in strong nitric acid the iron is totally unacted on; but if the acid become diluted till it has a density of 1·35, or less, it is liable to act upon the metal with uncontrollable violence. No combination possesses the intense energy, in union with convenience of working and comparative durability, in the same degree as that proposed by Grove. It is necessary, however, to place the nitric acid battery so that the nitrous fumes (which are copiously evolved during its action, especially after the battery has been in use for some time) shall pass at once into the open air; as they would otherwise seriously incommode the operator.

(267) *Smee's Battery.*—The other mode of obviating the counteracting agency of hydrogen upon the negative plate of the battery is less perfect, and is of a mechanical nature. It was first practically applied by Smee in the construction of the voltaic battery. Hydrogen adheres to smooth surfaces of platinum and

other metals with considerable force, but it passes off with ease from their asperities and edges: by multiplying their points and irregularities, as, for example, by the deposition of metal on the surface in a pulverulent form, the escape of the gas is much facilitated. Smee employs as the negative or conducting plate in his battery, a plate of silver, the face of which has been roughened by the deposition of finely divided platinum upon its surface; each side of the silver plate being exposed to a plate of zinc well amalgamated, and of equal extent, which acts as the positive plate. This pair of plates is excited by means of diluted sulphuric acid.

Fig. 221 represents a battery constructed upon Smee's principle: a thin platinized silver plate is supported in a light frame of wood, as shown detached

FIG. 221.



at s; to the upper part of this frame a binding-screw, in metallic connexion with the silver, is fastened, for the purpose of connecting the plate with the zinc plates of the adjoining cell, by means of a strip of sheet copper bent as at *c*; on either side of the silver plate a sheet of amalgamated zinc, z, z, is supported by the clamp shown at *b*; the zinc plates are prevented from contact with the silver plate by means of the wooden frame, and they are connected with the silver of the adjacent cell by a second binding-screw in the clamp shown at *b*; the separate plates are attached to a wooden frame, and being counterpoised by weights, as indicated in the figure, can be lowered into the trough of acid when wanted for use, or can be withdrawn from it when the experiment is over. The trough is divided into separate cells or compartments for each pair of plates, by glass partitions rendered water-tight by means of a resinous cement.

(268) *Resistances to the Voltaic Current.*—The current which circulates in any given circuit is not dependent solely upon the energy of the chemical action which is exerted between the generating metal and the exciting liquid. The current experiences a resistance from the very conductors by which it is transmitted; just as in the transmission of work, the intervention of the pivots and levers which are required for its conveyance intro-

duces additional friction, which requires to be overcome, and which thus diminish the efficient power of the machine.

The resistance to the voltaic current may be considered as of two kinds—first, that resistance which arises from the exciting liquid employed in the voltaic cell itself; and secondly, that which arises from the conducting wire and apparatus exterior to the voltaic cell. In a large number of cases the resistance offered by the exciting liquid is by much the most considerable, and it is inseparable from the combination; whilst the second source of resistance, or that which is exterior to the cell, can be increased or diminished at pleasure, and by the employment of very short and thick wires for connecting the plates, can be virtually removed altogether or annihilated. It will be advisable to consider first the resistance produced by the liquid in the active cell itself.

If plates of equal size be taken, the resistance occasioned by the liquid increases directly as the distance between the plates; the longer the column of imperfectly conducting matter which the current has to traverse, the greater is the difficulty which it will experience. If two plates be immersed in acid at the distance of an inch (25 millimetres) asunder, they will produce 10 times the effect that they would occasion at the distance of 10 inches or $250^{mm.}$ from each other. On the other hand, the larger the area of the plates that are immersed, the less is the resistance. For example, if a pair of plates, $25^{mm.}$ broad and $250^{mm.}$ long, be immersed in acid to the depth of $25^{mm.}$ only, the current produced will only be equal to one-tenth of that which would be obtained by immersing each plate for its whole depth of $250^{mm.}$ in the liquid. The resistance of the liquid is therefore directly as the distance between the plates, and inversely as the surface of the plates exposed to its action. A pair of plates exposing each a square centimetre of surface, immersed in acid at a distance of 1 centimetre apart, will consequently produce an effect equal to that which would be obtained from a pair of plates which each exposed a surface of 12 square centimetres to the action of the liquid, if they were 12 centimetres apart.

A case somewhat analogous is offered when water is transmitted through pipes. The greater the length of the pipe, the more considerable will be the friction and the consequent resistance to the passage of the liquid; whilst the larger the area of the pipe the more readily will the water escape. An aperture which exposes a sectional area of two square centimetres will, *cæteris paribus*, allow twice as much water to escape from it in

a given time as an aperture of which the superficial area is but a single square centimetre.

If the two plates are of unequal size, but are immersed parallel to each other, they may, for most practical purposes, be calculated as each exposing a surface equal to the mean surface of the two. Other circumstances independent of the extent of surface exposed by the plates, and the distance between them, materially influence the resistance of different liquids to the current. Any cause that favours chemical action between the active metal and the liquid, or which diminishes the chemical attraction by which the elements of the liquid are united, such as elevation of temperature, diminishes the resistance of the liquid. In most cases an increase in the concentration of the solution, provided its strength be not so great as to render deposition of crystals liable to occur, diminishes the resistance (278). The current likewise experiences a specific resistance in each liquid which depends upon the chemical attraction with which its particles are united together.

Similar, but distinct resistance, though to a less extent, is offered by the metallic part of the circuit. However great its conductivity may be, it always offers some obstruction to the current. The longer the wire employed, the greater is the resistance experienced by the current in traversing it. The resistance of each metal, like that of each liquid, is specific. Copper and silver, for instance, when wires of equal thickness and length are compared, offer far less resistance to a current of given amount than less perfect conductors, such as iron and lead. Experiment has demonstrated that with metallic conductors the same law holds good as with liquids—viz., that the resistance is directly as the length of the wire, and inversely as the area of its section. In cylindrical wires this sectional area will of course vary as the square of the diameter of the wire; for instance, a wire of $1^{mm.}$ in thickness will for equal lengths offer four times the resistance of a wire $2^{mm.}$ thick. If wires of the same metal, and of equal lengths, be compared, the resistance will vary inversely as the weights of the wires.

In the experiment with cupric sulphate (fig. 214), the metal is deposited in greatest quantity where the current is most readily transmitted—viz., in those points which are nearest to the zinc, and where the resistance offered by the liquid, which here forms the thinnest layer, is consequently the least.

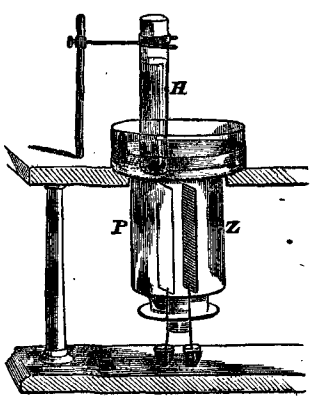
A rod of zinc supported within a cylinder of copper forms a convenient arrangement of the generating and conducting plates, because, when such a rod is placed in the axis of the cylinder,

the action is evenly distributed over the whole surface of the copper.

(269) *Difference between a Simple and a Compound Circuit.*—The observations hitherto made have referred to cases in which only a single pair of metals is employed. It will be necessary now to consider in what way the results are modified by the employment of several pairs of plates. It has already been stated when speaking of the electricity developed by friction, that when a large supply of electricity is needed, it may be obtained with equal effect either from a single Leyden jar which exposes a large extent of coated surface, or from a number of smaller jars which together expose the same amount of coated surface, all the inner surfaces of the small jars being in metallic communication with each other, but insulated from the outer coatings, all of which likewise are connected by some good conducting material (235). A similar result is also obtained in voltaic arrangements. Provided that the plates expose the same extent of surface and be kept at an equal distance apart, it matters not whether they be immersed in a single vessel of liquid, or whether they be cut up into strips and be immersed in pairs in separate vessels of the same liquid. The only requisite is that all the zinc plates shall be connected together by stout metallic wires, and that all the platinum plates shall be similarly connected by other wires. No action will occur until metallic communication between one of the platinum and one of the zinc plates is effected by means of a conducting wire: and then the whole force of the united plates will traverse the connecting wire.

These results may be exhibited to the eye in the form of battery in which the hydrogen evolved from each platinum plate admits of being collected—a contrivance proposed by Daniell, which he called a *dissected battery*. Fig 222 shows the manner of mounting one of these cells. When in use the cells are charged with the diluted sulphuric acid, and a small graduated jar, H, also filled with the diluted acid, is inverted in each of the cells over the platinum plate, P, in such a manner as to receive the hydrogen which is disengaged during the operation. The plates of such a battery can easily be connected

FIG. 222.



so that all the plates of zinc, z, shall be united by conducting wires, and all the platinum plates in a similar way by other wires; or they can with equal readiness be united so that the zinc of one cell shall be connected with the platinum of the following cell. Suppose, for instance, two plates (z and p, fig. 223), one of zinc, the other of platinum, each six inches square, be immersed in a vessel of sulphuric acid, at a distance of an inch apart. A current of a certain intensity will be obtained on connecting the two plates by means of a wire, w; and in five minutes a certain quantity of zinc will be dissolved, whilst a corresponding quantity of hydrogen gas will escape from the platinum. Now if the zinc and the platinum be each cut into strips of an inch broad and six inches long, and the several pairs of zinc and platinum strips be immersed in separate vessels of diluted sulphuric acid at the distance of one inch from each other, and if, as in fig. 224, all the zinc strips, z, z, be connected by wires, and all the

Fig. 223.

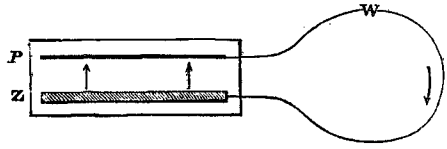
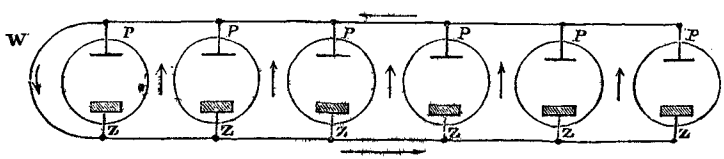


Fig. 224.

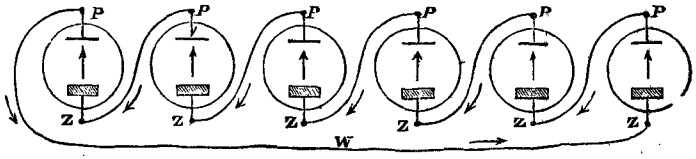


platinum strips, p, p, be similarly united,—on connecting them together by a wire, as shown at w, the same current will traverse the wire as in the first combination, and the quantity of zinc dissolved in the six plates taken together will in five minutes be the same as that which was dissolved from the single zinc surface in the first arrangement; whilst the quantity of hydrogen gas which will rise from all the six plates of platinum together will be equal to that obtained from a single plate in the former experiment (fig. 223). Such a combination, in whichever of the forms just described it be employed, may be regarded as a single pair of plates, and it constitutes a *simple voltaic circuit*.

By acting upon extensive surfaces arranged in simple circuits, the *quantity* of electricity which can be thrown into circulation is very large, though its *intensity*, that is to say, its power of overcoming resistance, is comparatively small.

The results would, however, be altered if, instead of connecting the divided plates together in the manner represented in fig. 224, they were connected as in fig. 225, in which the zinc in each

FIG. 225.



cell is supposed to be connected with the platinum plate of the adjacent cell in regular order through the series. When the extreme plates are connected by a thick wire w, the current which traverses this wire in a given time is equal to one-sixth only of the current which was thrown into circulation in the former instances; but the quantity of zinc dissolved in the six cells taken together is the same as before: and if the hydrogen be collected from the six platinum plates, the quantity will be still equal to that disengaged in the experiments shown in figs. 223 and 224. The current has now to traverse each cell of the liquid in succession, and thus has to encounter a great additional resistance. Yet now the current starts from six separate points of origin, and each of these separate points adds its energy in driving forward the current. The electro-motive force is increased sixfold, whilst the resistance of the liquid is increased still more; in the first place it is increased sixfold from the circumstance that the length of the column of liquid which must be traversed, is six times as great, and it is next further increased sixfold by a proportionate diminution in the breadth of the column. In the arrangement of fig. 224 there was a column of liquid six inches wide and one inch thick to be traversed; whilst in the arrangement of fig. 225 there is a liquid column six inches thick and only one inch wide to be traversed. When the plates are arranged in separate compartments, and are connected together alternately, as in fig. 225, they constitute a *compound voltaic circuit*. Volta's pile (fig. 210) and his crown of cups (fig. 211) are therefore compound circuits, and it is this form of combination which enabled him to obtain results so much superior to those of any previous experimenter. The electricity in this case is not greater in quantity than that obtainable from a simple circuit; nay, it is often much less; but it has a much higher intensity, and its power of overcoming resistances is very much greater, as a further examination will show. If, for example, 50 or 100 miles of wire, such as is used

for telegraph purposes, be introduced in a combination arranged, as in fig. 224, as a simple circuit, the effect obtained would be very materially less than if the same plates were arranged in the form of a compound circuit, as shown in fig. 225.

(270) *Ohm's Theory.*—These considerations may be much simplified, by representing the mutual action of the electro-motive forces and the resistances of any circuit, simple or compound, in the form of a fraction, in the way proposed by Ohm.

It has been found by experiment that the quantity of electricity produced by any combination is directly proportioned to the electro-motive force, or chemical energy between the active metal and one of the elements of the liquid upon which it acts; and inversely proportioned to the resistances to be overcome. The numerator of the fraction will therefore be represented by E, the electro-motive force, and the denominator by $R+r$; where R represents the resistance in the cell or the battery (due chiefly to the attraction between the elements of the liquid for each other), and r all resistances exterior to the cell or the battery, such as the connecting wire: thus the expression $\frac{E}{R+r}=A$, would represent the effect of any combination where A indicates the quantity actually in circulation, whether measured by its heating or by its magnetic effects. If the connecting wire be very thick, so as to offer little or no resistance to the current, r becomes evanescent, and the fraction assumes the form of $\frac{E}{R}=A$; the current under these circumstances is proportional to the surface of the plates exposed to the action of the liquid.

Let it be assumed, for example, that $E=1$, and that $R=1$, when a pair of zinc and platinum plates an inch broad and six inches long is immersed in diluted acid at the distance of one inch asunder, so that under these circumstances, $\frac{E}{R}=\frac{1}{1}=1$. If a pair of plates six inches broad and six inches long, also at a distance of one inch apart, be immersed in the same acid, since the resistance is inversely as the surface of the plates immersed, the fraction becomes $\frac{E}{\frac{R}{6}}$ or $\frac{1}{\frac{1}{6}}=6$; or the current is increased sixfold as compared with the former. If the plates be each cut into six similar strips, and be then arranged in pairs, as represented in fig. 224, the same fraction still represents the result, since the relative size and distance of the plates remain unchanged: but if the plates be arranged in succession, so as to produce a compound circuit, as in fig. 225, the fraction becomes $\frac{6E}{6R}=\frac{6}{6}=1$; the electro-motive force is increased sixfold, but the resistance is increased also in exactly the same proportion. The quantity which under

these circumstances circulates through the connecting wire is not greater than if a single cell only, containing a pair of plates one inch broad and six inches long were employed.

But suppose now that several miles of wire, such as are employed in telegraphic communication, be introduced into the two combinations severally represented in figs. 224 and 225; r now acquires importance;—let this resistance r be twentyfold greater than that of the liquid in each cell. In the first case (with the simple circuit), the fraction becomes $\frac{E}{\frac{R}{6}+r}=\frac{1}{\frac{1}{6}+20}=0{\cdot}049$; in the second (the compound circuit), the fraction is $\frac{6E}{6R+r}=\frac{6}{6+20}=0{\cdot}23$: so that although in both cases the resistance introduced most materially diminishes the current which enters into circulation, the quantity in the compound circuit is now five times as great as that which emanates under these circumstances from the simple circuit. Indeed, in all cases where great resistances external to the battery have to be overcome, a compound battery has a great advantage over the simple circuit.*

(271) *Chemical Decomposition.*—It is important to remember that the current which circulates through each cell in a compound circuit is not increased by the arrangement, if the connexion between its extremities be made by means of a good conductor; if, for example, 50 similar and equal cells be connected in succession, and be united by a stout short wire, the quantity of zinc which would be dissolved in a given time in each of these cells would not be greater than that which would be consumed in a single cell of the same size in the same time, if the plates which compose it were connected by a short thick wire.

The power of a compound circuit is shown in a striking manner when some liquid such as diluted sulphuric acid is interposed in the course of the conducting wire. The experiments

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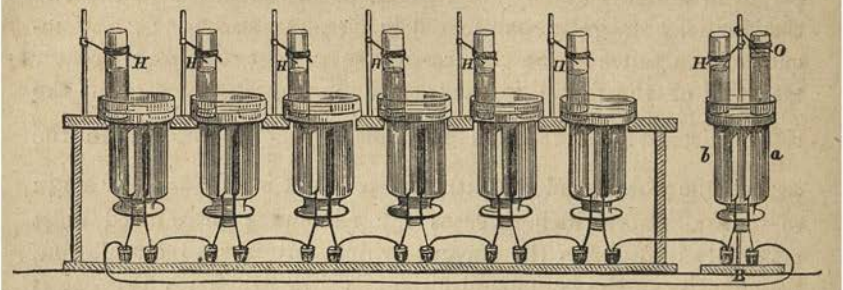
* Let n = the number of the plates in a compound circuit,
„ E = the electro-motive force.
„ D = the distance between the plates.
„ S = the area of the plates.
„ l = the length of the conducting wire.
„ s = the area of a transverse section of the wire.

The fraction which represents the action of a compound battery when its extremities are connected by means of a metallic wire of uniform diameter is the following: $\frac{\frac{nE}{nD}}{\frac{}{S}+\frac{l}{s}}=A$. In this expression $\frac{D}{S}$ is substituted for R, (the resistance in each cell of the battery) to which it is equivalent; since R is directly as the distance between the plates, and inversely as their area, or surface, while $\frac{l}{s}$ represents r.

which elucidate this point may be instructively performed by means of the dissected battery. If a pair of platinum plates, *a*, *b*, fig. 226, be immersed in the acid conducting-liquid at B, and

FIG. 226.



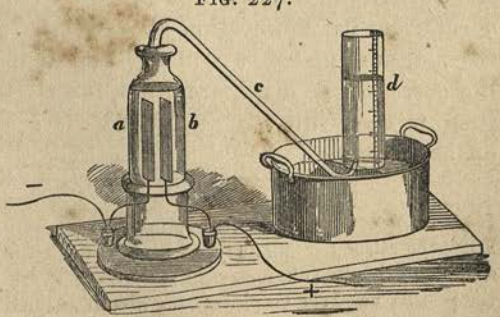
connected with the wires proceeding from the compound circuit in the manner represented in the figure, the liquid will be decomposed, oxygen will be given off from one plate, *a*, and will rise in the tube O; whilst hydrogen will be given off from the other plate, *b*, and may be collected in the tube, H; but if the same cells be arranged as a simple circuit, fig. 224, no such effect is produced. By the introduction of the liquid conductor at B, the resistance is very greatly increased, such a resistance being more considerable than that of many miles of wire. But this is not all: besides this resistance, a new counteracting electro-motive force shows itself, which gives rise to a current operating in a direction the reverse of that in the battery. This force is due to the oxygen and hydrogen which are separated upon the platinum plates, and which, as has been explained when speaking of the gas battery (264), is very considerable. Experiment shows that it is between two and three times as powerful as the electro-motive force of a pair of zinc and platinum plates excited by diluted sulphuric acid. When, therefore, the endeavour is made to decompose the diluted acid by a single pair of zinc and platinum plates, however large a surface they may present to the action of the exciting liquid, no visible action in the cell, B, ensues; a momentary decomposition, too small in amount to be perceived by the eye, produces a development of oxygen and hydrogen upon the two platinum plates, *a*, *b*, sufficient to oppose an effectual barrier to the transmission of the current. Even when two pairs of zinc and platinum plates are used, the energy of the current is insufficient to effect any visible decomposition; with three pairs a few bubbles of gas show themselves; and with a more numerous series, the effects increase rapidly, till at length a point is gained, beyond which no

advantage is obtained by increasing the number of cells in the battery.

It is particularly worthy of remark, that in every cross section of any voltaic circuit at a given instant, the quantity of electricity which traverses it is uniform: consequently, the same quantity of hydrogen makes its appearance upon the plate, *b*, of the cell B, which contains the liquid for decomposition, as is disengaged and collected during the same interval from each plate in the battery itself. If each zinc plate of the battery be weighed before the experiment is begun and after it is concluded, it will be found that each plate has lost weight to an equal extent. The interposition of the liquid at B may occasion a great reduction in the amount of electricity which is thrown into circulation: but at every transverse section of the battery, the electricity that does circulate is uniform in quantity; and the measurement of the chemical action, whether it be estimated by the quantity of gas which is evolved at any one point, or by the quantity of zinc which is dissolved, may be employed as a sure indication of the quantity of electricity in circulation: in other words, retardation of the current by the liquid conductor is necessarily attended with an equal retardation in the conducting wire, and in each cell of the battery itself.

(272) *The Voltameter.*—The foregoing important law was discovered by Faraday. As one of its consequences he was enabled to employ a decomposing cell, such as is shown at B, fig. 226, as a measure of the voltaic power of any circuit: such an instrument is called a *Voltameter*. For each 65 milligrammes of zinc dissolved in any one cell of the battery, 18 milligrammes of water are decomposed in the voltameter; whilst 22·32 cubic centimetres or 2 milligrammes of hydrogen, and 11·16 cubic centimetres or 16 milligrammes of oxygen, at 0° C. and 760$^{mm.}$ Bar., are evolved upon its plates; at the same time 22·38 cubic centimetres of hydrogen are evolved from every platinum plate in the cells of the battery. A more convenient form of voltameter is shown in fig. 227. It consists of an upright glass cell, to the neck of which a bent tube, *c*, for the conveyance of

Fig. 227.



the disengaged gases, is fitted by grinding; the vessel is filled with diluted sulphuric acid; *a*, *b*, are the two platinum plates, each of which is connected by a wire which passes through the foot of the instrument, to a mercury cup, by means of which communication can be made with the wires which convey the current from the battery: oxygen and hydrogen are liberated by the action of the current upon the acidulated water, both gases then rise to the surface of the liquid, and are conveyed by the bent tube, *c*, to the graduated jar, *d*, which stands in a small pneumatic trough.*

It is to be observed that the action of a simple zinc and platinum battery is not steady; it gradually declines, and before the acid has become saturated with zinc, the current almost ceases. On breaking the contact of the conducting wire with the two ends of the battery, and allowing it to remain disconnected for a few minutes, the action is partially restored; but it again gradually declines after the circuit has been completed. These effects were traced by Daniell to the action of the current upon the zincic sulphate, which is formed in each cell of the battery during the operation; the zinc salt is decomposed in the manner shown in the subjoined diagram, in which $ZnSO_4$ represents the zincic sulphate, and Pt and Zn the platinum and zinc plates of the cell. The brackets placed above the symbols indicate the arrangement of the particles before the current passes; those below show the change produced by the voltaic action:—

$$\underbrace{\overbrace{Pt\ Zn}\ \overbrace{SO_4\ Zn}\ \overbrace{SO_4}}\ \underbrace{Zn}$$

In this manner metallic zinc becomes reduced or deposited upon each platinum plate, and the power of the battery is arrested when the two surfaces which are opposed become virtually zinc and zinc instead of platinum and zinc. This evil may be obviated by interposing a porous diaphragm between the two plates, as in the batteries of Daniell and of Grove (265, 266); in these cases a sufficient communication between the zinc and the copper or the platinum plates, is still kept up by means of liquid through the pores of the diaphragm, but the zincic sulphate is prevented from mixing with the liquid which is in contact with the copper or the platinum.

* At low temperatures the proportion of oxygen evolved is always a little below the calculated quantity, owing to the retention of a small quantity by the acid liquid in the voltameter, in the form of hydric peroxide (H_2O_2): the larger the positive electrode employed, the greater is the diminution of the oxygen.

(273) *Further Application of Ohm's Theory.*—All the phenomena of compound circuits admit of ready calculation by the application of Ohm's law; for instance, if n represent the number of the plates, the expression for any compound series, the cells of which are similar in nature and equal in size, becomes $\frac{nE}{nR+r}=A$; since in each cell not only is a new electro-motive force introduced, but at the same time a new resistance. Provided that the exterior resistance is such as would be offered by a metallic wire which may be even many miles in length, it is possible exactly to double the current by doubling the number of cells, if at the same time the size of the plates be doubled; for $\frac{2nE}{\frac{2nR}{2}+r}=\frac{2nE}{nR+r}$. But if, when the number of cells is doubled and the surface of the plates also is doubled, a voltameter be employed to measure the current, instead of introducing a wire as the exterior resistance, the current measured by the voltameter is not found to be doubled, as might naturally have been expected: this difference arises from the counter current which is produced in the voltameter itself, by the accumulation of the oxygen and hydrogen upon its plates. Call this counter current e, and the formula becomes $\frac{nE-e}{nR+r}$.

The values both of e, (the counter current offered by the voltameter,) and r, which, if short thick conducting wires be used, is virtually the resistance of the voltameter itself, may be very simply estimated in the way proposed by Wheatstone. This method consists in comparing two experiments in which the resistances remaining the same, the electro-motive forces alone vary. Upon the supposition that the voltameter merely offers an increased resistance without introducing any counteracting electro-motive force, five single cells should produce a result equal to half that obtained by the use of ten cells of double size; but by experiment, the effects as measured by the voltameter are as 6 : 20. Comparing these effects with the arrangements which produce them, we obtain the following proportion, from which the value of e is deduced in terms of E:—

$$\frac{10E-e}{\frac{10R}{2}+r} : \frac{5E-e}{5R+r} :: 20 : 6\text{; therefore } e=2\tfrac{6}{7}E.$$

The resistance r of the voltameter may be calculated with equal ease; for taking two similar batteries, each composed of ten cells, but in one of which the plates are exactly double the size of those in the other, the electro-motive forces will continue the same while the resistance alone will vary. Under these circumstances the experimental results, furnished by the voltameter in equal

times, were as 12·5 : 20; and $\frac{10E-e}{10R+r} : \frac{10E-e}{\frac{10R}{2}+r} :: 12{\cdot}5 : 20$; therefore $r=3\frac{1}{3}R$. By substituting in the formula the values for e and r thus obtained by experiment, the results for any given number of cells may be calculated; and on comparing the values obtained by such calculation with the numbers furnished by actual experiment, Daniell (*Phil. Trans.* 1842, 146) obtained the following results:—

Number of Cells.....	3	4	5	10	15	20	
Gas calculated.....	$\frac{5}{8}$	$3\frac{3}{5}$	6	$12\frac{1}{2}\frac{2}{5}$	$15\frac{2}{2}\frac{1}{5}$	$17\frac{1}{2}\frac{2}{5}$	Cubic in.
Gas observed	$1\frac{1}{8}$	$3\frac{7}{8}$	6	$12\frac{1}{2}$	$15\frac{3}{4}$	$17\frac{1}{2}$	Cubic in.

Any alteration in the size of the plates of the voltameter necessarily alters the resistance which it offers to the current, and the influence of this change in the voltameter is most perceptible when a battery consisting of a few plates which expose a large surface is employed.

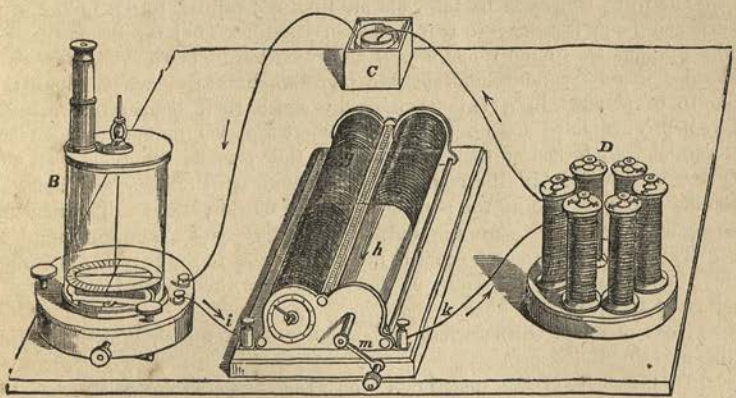
The preceding considerations will render it evident that no general answer can be given to the question, 'What number of cells should a battery contain in order that it may produce the greatest current?' The electro-motive force, E, varies in amount with the kind of battery which is used; the values for R and r will also vary with the varying circumstances of the experiment. It is found that every different arrangement requires the employment of a distinct number of cells in order to obtain from it the maximum effect with the least expenditure of zinc. This number will vary even with the same form of battery, according to the size of the battery plates, the length of wire in the circuit, and the nature of the liquid conductor in the decomposing cell. It may be stated, however, as a general principle, that the most advantageous effect is obtained when the value of A, in the formula $\frac{nE-e}{nR+r}=A$, most nearly approaches 0·5, E and R each being=1: in other words, the advantage is greatest when the exterior resistances—viz., those of the conducting wire and voltameter together—are equal to the sum of the resistances due to the battery itself; it may therefore be concluded that when the exterior resistance is trifling, as usually occurs when the circuit is metallic and not of very great length, little or nothing is gained by employing a large number of cells; two or three plates of large surface being the best under such circumstances; but that where a considerable chemical resistance is to be overcome, power is gained by employing a series numerous in proportion to the resistance so intro-

duced. In no case, however, is it possible by the use of a series of plates of uniform dimensions, even if of unlimited number, to produce in any transverse section, such as an included voltameter, a chemical action greater in amount than that which would occur in a single cell of the arrangement in which the circuit was completed by a stout metallic wire.

(274) *Wheatstone's Rheostat and Resistance Coils.*—Guided by the principles which have just been explained, Wheatstone (*Phil. Trans.* 1843, 303) contrived an apparatus termed the *Rheostat*, by which measured amounts of resistance may be introduced into the voltaic circuit: if the effect which such added resistance has upon the amount of the current in circulation be measured, the different values of E, R, and r in different arrangements, may be deduced by a simple calculation.

The rheostat is represented in fig. 228: g is a cylinder of well-baked wood, $1\frac{1}{2}$ inch (4 centimetres) in diameter and 6 inches (15 centimetres) in length; it turns easily upon a horizontal axis: on this cylinder a spiral groove is cut, the thread of which contains 40 turns to the inch. This groove runs from one end of the cylinder to the other, and in it is coiled a brass wire $\frac{1}{100}$ inch ($0{\cdot}25^{mm.}$)

FIG. 228.



in diameter; h is a brass cylinder, placed parallel to g, and equal to it in diameter; the thin wire upon g is connected at the end i with a brass ring, and at the other extremity is attached to the cylinder h; at i is a metallic spring, one end of which is connected with a binding screw, and the other end of which rests against the brass ring, and effects the communication with one wire of the battery: m is a movable key, by which the wire can be wound upon the brass cylinder, or by transferring the key to the axis of g, it can be unwound from h, and returned to the wooden cylinder, g. In consequence of the non-conducting quality of dry wood, the coils of wire on the wooden cylinder are insulated from each other, so that the current traverses the whole length of the wire coiled upon this cylinder, but the coils not being insulated from each other on the brass cylinder, the current immediately passes from the point of contact to the brass spring at k, which is in communication with the other wire from the battery.

A scale is placed between the two cylinders for the convenience of counting the number of coils unwound, and the fractions of a turn are read off upon a graduated circle, which is traversed by an index attached, as is shown in the figure, to the axis of the cylinder, *g*.

Wheatstone took as his standard of resistance, the resistance produced by a copper wire 1 foot of which is exactly 100 grains.* It is sometimes necessary to be able to introduce an amount of

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* The conductivity of copper, however, varies so greatly, owing to the presence of slight impurities, that it is unfitted for this purpose (p. 559). The question of a standard of resistance has been made the subject of a series of laborious investigations by a committee of the British Association, and in 1865 they issued a report from which we extract the most important conclusions (*Brit. Association Report*, 1865, 308). It will be seen that they consider that the problem is practically solved:—

"The Report for the year 1864 announced the completion of the experiments determining the resistance in absolute measure of a certain coil of German-silver wire. Taking this coil as the basis, Dr. Matthiessen, assisted by Mr. C. Hockin, prepared ten standards, each expressing the British Association unit of electrical resistance; two of these standards are coils of platinum wire, two are coils of wire drawn from a gold-silver alloy, two are coils of wire drawn from a platinum-iridium alloy; and the remaining two are tubes of mercury.

"The wires employed in the coils are from 0·5 millim. to 0·8 millim. diameter, and range from one to two metres in length. They are insulated with white silk, and are wound round a long hollow bobbin of brass. The wires are imbedded in solid paraffin, and enclosed in a thin brass case, which allows the coils to be plunged in a bath of water by which their temperature may be conveniently regulated and observed. Two short copper terminals project from the case and are forked at their ends, so that they may be connected with the Wheatstone's balance in the manner recommended by Professor W. Thomson, avoiding the error due to the possible resistance of connexions. The mercury standards consist of two glass tubes about three-quarters of a metre in length.

"These ten standards are equal to one another and to the British Association unit, at some temperature stated on the coil or tube, and lying between 14°·5 and 16°·5 C.

"None of them, when correct, differ more than 0·03 per cent. from their value at 15°·5 C.

"In the choice of the material of which the standards are constructed, the committee have been much assisted by the experiments on permanency made by Dr. Matthiessen.

"Silver and copper were found to alter in their resistance simply by age. German silver was also found to alter in some cases.

"These materials had therefore to be rejected. Gold appears constant, but owing to its low specific resistance a considerable length would have been required, unless a wire had been adopted of very small diameter. This was not thought desirable, for several reasons; any slight decay or injury in the surface of a small wire would cause much greater alteration in the resistance than the same injury to a large wire. A small wire would be more liable to mechanical injury, and would be much more rapidly heated by the passage of currents. The committee having rejected small wires for these reasons, thought it unnecessary to incur the expense of a large and thick gold wire. The great change of resistance caused by a change of temperature furnished another reason for

resistance into a circuit much greater than can be effected by means of the rheostat. For this purpose Wheatstone employed the *Resistance Coils*, shown at D, fig, 228. These coils are composed of fine copper wire $\frac{1}{200}$ of an inch ($0{\cdot}127^{mm.}$) in diameter, carefully insulated by covering them with silk; two of the coils

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rejecting gold and other pure metals. One pair of standards was, however, made of platinum, which appeared the most suitable of all the pure metals. Platinum and the three alloys named appear all to be very constant, that is to say, their resistance is not altered by age, or even by being subjected to considerable heat and recooled.

"These materials also possess considerable mechanical strength; they are not easily injured by chemical action, they have considerable specific resistance, and that resistance, in the case of the three alloys, changes little with a change of temperature.

"It is of course impossible to say with certainty that their resistance will not vary with time, but it is most unlikely that the resistance of all will vary in the same ratio. . . . . .

"Dr. Siemens was the first person who produced numerous sets of coils accurately adjusted; and although unable to recommend the adoption of his unit of resistance, the committee once more take an opportunity of expressing their sense of the high value of Dr. Siemens's researches on the reproduction of units by means of mercury. Dr. Siemens is confident that a unit can be and has been reproduced by means of mercury with an accuracy of 0·05 per cent.; but meanwhile, the chief security for the permanency of the unit consists in the preservation of standards constructed in various ways and of various materials.

"The mercury tubes furnish an additional security. A molecular change may occur in the wires, that is to say, they may become of harder or softer temper, they may be injured chemically in course of time by some action on their surface; it is just possible that the repeated passage of currents may alter them in some way, although we have no reason as yet to expect such an alteration.

"Mercury is free from all these objections. Its temper cannot vary, and as it would be purified afresh on each occasion, it will be chemically uninjured.

"On the other hand, some fresh dangers may occur in its use. The tubes themselves may alter in time, or the mercury may not always be absolutely pure. Absolute security cannot be had, but the choice of a variety of materials will probably prevent any serious alteration from occurring without detection.

"The copies which have been issued are similar in form to the standard coils, but the terminals are simple thick copper rods, intended to be dipped in mercury cups. The security given by this mode of connexion is sufficient for all ordinary purposes, and it was feared that the use of the double terminals might not be everywhere understood. The platinum silver alloy has been used in all the copies. Wire made of this alloy is very strong and ductile. It can, for instance, be drawn down to a diameter of 0·0002 inch. Its resistance is not permanently altered even by a great change of temperature, and even annealing hardly affects it. Moreover, the change in its resistance, due to a variation of 1° C., is at ordinary temperatures only 0·032 per cent., being less than that of any other alloy tested. It is also a commercial alloy, which has been long used by dentists."

are 50 feet in length, the others 100, 200, 400, and 800 feet long. The ends of each coil are attached to short thick wires, fixed to the upper faces of the cylinders, which serve to combine all the coils into one continued length of 1600 feet (487·67 metres) of wire. Two wires proceed from the extremities of the coils by which they are united to the circuit. On the upper face of each cylinder, is a double brass spring, movable round the centre, so that its ends can be made to rest upon the thick brass wires, or can be removed from them at pleasure. When the spring rests upon the wires, the current passes through the spring instead of through the coil; but when the spring rests upon the wood, the current must pass through the coil. In the figure, all the springs are shown as resting upon the wires: in this case none of the coils are included in the circuit, but by turning the spring of any particular coil, 50, 100, 200, or 400 feet of wire can, in a moment, be introduced into the circuit.

The following is Wheatstone's description of his method of ascertaining the sum of the electro-motive forces in any voltaic circuit or circuits:—

'In two circuits producing equal electro-motive (or voltaic) effects, the sum of the electro-motive forces, divided by the sum of the resistances is a constant quantity; *i.e.*, $\frac{E}{R}=\frac{nE}{nR}$: if E and R be proportionately increased or diminished, A will obviously remain unchanged. Knowing, therefore, the proportion of resistances in two circuits producing the same effect, we are able immediately to infer that of the electro-motive forces. But as it is difficult in many cases to determine the total resistance, consisting of the partial resistances of the *rheomotor* [or voltaic combination] itself, the galvanometer, the rheostat, &c., I have recourse to the following simple process:—Increasing the resistance of the first circuit by a known quantity, r, the expression becomes $\frac{E}{R+r}$. In order that the effect in the second circuit shall be rendered equal to this, it is evident that the added resistance must be multiplied by the same factor as that by which the electro-motive forces and the original resistance are multiplied; for $\frac{E}{R+r}=\frac{nE}{nR+nr}$. The relations of the length of the added resistances r, and $n\,r$, which are known immediately, give therefore those of the electro-motive forces.'—(*Phil. Trans.* 1843, 313.)

Suppose, for example, it be desired to compare the electro-motive force obtained from a single pair of zinc and copper plates in one of Daniell's cells, with that of two pairs of the same combination, the following will be the mode of conducting the experi-

ment:—Interpose the rheostat (fig. 228) and the galvanometer, B, in the circuit obtained from the single cell, C; then, by coiling or uncoiling the wire of the rheostat, bring the needle exactly to 45°. Next uncoil the wire of the rheostat, and count the number of turns required to bring the needle to 40°. Suppose 35 turns are required: this number of turns may be taken to represent the electro-motive force of the combination. Now introduce the two cells, arranged as a compound circuit, instead of the single cell at C. Bring the needle as before to 45°, interposing one or more of the resistance coils at D, if needed, by turning the spring upon the wood of the reels, and complete the adjustment by coiling or uncoiling the wire of the rheostat. Again uncoil the wire of the rheostat until the galvanometer needle stands at 40°. Seventy turns, or twice the number previously required to produce this effect, will now be needed. The electro-motive forces in the two cases are therefore as 35 to 70, or as 1 : 2. If instead of arranging the two cells as a compound circuit the zinc plate be connected with the other zinc plate and the copper with the copper, so as to form a single circuit, it would have required the interposition of a greater resistance to reduce the needle to 45° to start with than when one cell only was used; but only 35 turns of the rheostat would be needed to bring the needle down to 40°. This last experiment shows that the electro-motive force is not altered by increasing or diminishing the size of the plates.

The electro-motive force of any combination may by means of this arrangement be compared with any one selected as a standard: it was in this way that the results on the comparison of the electro-motive effects of platinum, zinc, and potassium (260) were obtained.

Processes of Voltaic Discharge.

(275) Having now reviewed the principal circumstances which influence or exalt the activity of the voltaic battery, we may proceed to examine the phenomena which are manifested when a powerful combination is brought into action by connecting its opposite extremities. Voltaic action is exhibited only during the process of discharge, for the current is a continuous succession of discharges of the electricity developed and maintained by the contact and chemical action of the materials employed in the construction of the battery. The discharge of the voltaic battery may, like that of the ordinary machine, be considered under three heads—viz., the discharge by *conduction*, as when the circuit is completed by a wire or other good solid conductor; the discharge

by *disruption*, in which case a luminous appearance is exhibited through a short interval of non-conducting matter; and the discharge by *convection*, which takes place in liquids, and is accompanied by chemical action and transference of the particles of the conductor.

(276) *Conduction.*—In all cases where electricity is in motion, whether it be excited by chemical action, as in the voltaic pile, or by friction, as in the common electrical machine, the current is conveyed by the entire thickness of the conductor; the electricity is not confined to the surface, as occurs when the electricity is at rest, and produces effects by induction only. In the case of the voltaic current as well as in the momentary discharge of the Leyden battery, by far the greater portion of the induction occurs between one transverse section of the conductor and the adjacent sections immediately before and behind it; and but a small portion of the induction, sufficient however to be distinctly manifest, is diverted to surrounding objects. By reducing the thickness of the conducting material, a large quantity of the current is compelled to traverse a given number of conducting particles in the same time, and a great elevation of temperature is thus produced. The heat may rise sufficiently high to cause ignition of the wire, and this ignition may be produced at any point of the circuit, so as to produce the explosion of a charge of gunpowder sunk in the depths of the ocean or buried within the recesses of a mine; the operations of blasting may thus be made to assume a degree of certainty and of safety hitherto unattained by other means, since the moment at which the discharge shall take place is absolutely under control.

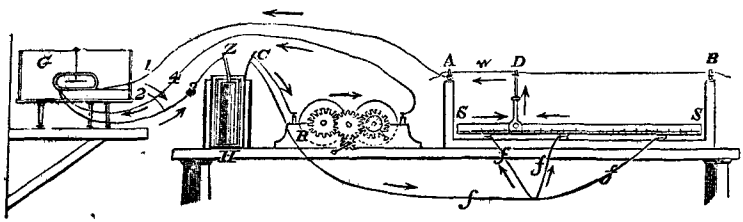
Elevation of temperature diminishes the conductivity of the metals: a good experimental proof of this fact is afforded by transmitting through a platinum wire a voltaic current of sufficient strength to raise the wire to a dull red heat; and whilst the current is still passing, igniting a loop of the wire in the flame of a spirit lamp; the temperature of the other part immediately falls, owing to the diminished quantity of electricity which traverses it, in consequence of the increased resistance offered to the passage of the current by the strongly ignited part of the wire. If a loop of the wire be cooled by immersion in water, the opposite effect is produced; for in this case the reduction of temperature at one point enables a larger current of electricity to pass through the wire, which may thus be raised to a heat approaching its point of fusion. The power of a voltaic combination may be roughly estimated by the number of centimetres of platinum wire of uniform diameter,

which it will heat to redness: the same quantity of electricity is transmitted in equal intervals of time through wire of the same temperature, whether it be a centimetre only or a metre or more in length: but the increased length which the stronger current will ignite measures the increase in tension of the electric discharge. Dr. Siemens has constructed a thermometer depending on the diminution of the conductivity of a platinum wire by a rise of temperature (*Proc. Roy. Soc.* 1871, xix. 443).

The conductivity of the different metals for electricity varies nearly in the same order as their conductivity for heat; but it is remarkable that charcoal, though so bad a conductor of heat, transmits electricity with great facility. The measurement of the conductivity of solids and of liquids for electricity has occupied the attention of many distinguished philosophers. An ingenious method was proposed many years ago by Becquerel, who constructed a *differential galvanometer*, in which the needles were surrounded by two insulated copper wires of equal length and diameter; they were coiled in the usual way, and formed two independent circuits, so that the galvanometer had four terminations instead of two. When two perfectly equal currents were transmitted, one through each wire in opposite directions, they exactly neutralized each other in their effect upon the needle, which therefore remained stationary; but if either current preponderated, a corresponding deviation of the needle was occasioned. To use the instrument, a small voltaic combination was connected with the galvanometer, two wires passing from each pole, so as to divide the current into two exactly equal portions, one being transmitted through one of the coils, the other through the second coil in the opposite direction. Wires of the different metals were then introduced into the two circuits. If into either circuit a conductor of inferior power were introduced, the current in that circuit was proportionately diminished, and the needle was disturbed; but the equilibrium could be restored by increasing the length of the wire in the other circuit; then by comparing the lengths of the two wires thus introduced, their relative conductivity could be inferred. By means of this instrument, conjoined with the use of Wheatstone's rheostat, Ed. Becquerel was enabled to measure the conductivity of a number of wires of different metals with precision (*Ann. Chim. Phys.* 1846 [3], xvii. 242). The relative conductivities of the wires were obtained by ascertaining the lengths of the rheostat wire, which was required to restore the equilibrium, when wires of different metals were employed. In fig. 229 is exhibited the arrangement adopted

in these experiments. G is the differential galvanometer with its four wires, 1 and 3 being the terminations of one coil, 2 and 4 those of the other coil; H, a voltaic pair; R, the rheostat; and *w*, the metallic wire the resistance of which is to be measured. This wire is stretched and insulated between two binding clamps, A and B; S S, is a copper scale, with linear subdivisions for measuring the length of the wire which is included in the circuit; D is a sliding

FIG. 229.



clamp of copper, which can be made to move in either direction along the scale S, and can be connected with *w*, at any desired point, by the clamp at D. Suppose the resistance of a certain length of the wire *w* is to be measured. The current from H is divided into two portions so as to send each in opposite directions through the galvanometer. One half of the battery current is made to pass along the wire *f f f*, up the clamp D, and through part of the wire *w*; the other half is transmitted through the rheostat, in the direction shown by the arrows. By coiling or uncoiling the wire of the rheostat, the two circuits are rendered exactly equal, so that the needle of the galvanometer shall stand at 0°. Now, if D be unclamped, and it be caused to slide through a definite distance, say $300^{mm.}$ towards B, the equilibrium of the galvanometer will be destroyed; since the resistance in *w* is increased, whilst that in the rheostat remains unaltered; but by uncoiling the wire of the rheostat, additional resistance can be introduced into the circuit of which it forms a part; the equilibrium may thus be again restored, and the resistance of $300^{mm.}$ of *w* will be given by counting the number of coils of the rheostat required. The comparative resistances of any number of different wires introduced at *w* may thus be readily ascertained.

The following table exhibits the conductivities of wires of equal length and diameter of various metals as determined by this process. The mercury was placed in a glass tube of uniform diameter.

These metals were carefully purified and well annealed. It was found that annealed metals conducted better than those which

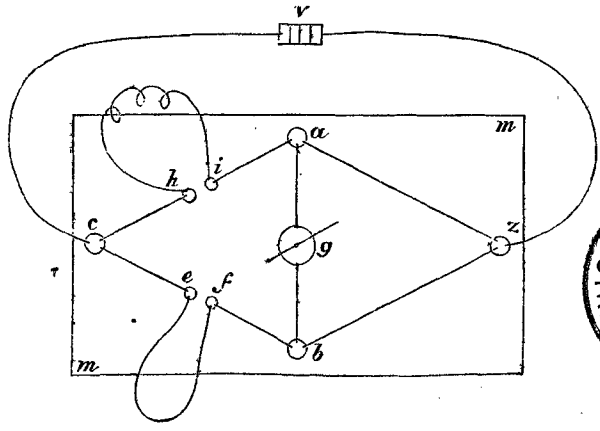
had not undergone this process. If hard drawn silver, for instance, have a conductivity of 100, the same wire when annealed will have a conductivity of 108·57 (Matthiessen). The effect even of a moderate elevation of temperature in reducing the conductivity for the time being is very considerable, as will be evident by comparing the second column of figures in the table with the first.

Electric Conductivity of Metals. (*E. Becquerel, Ann. Chim. Phys.* 1846 [3], xvii. 266.)

Metals employed.	At 0° C.	Conductivity at 100° C.		Loss per cent. each metal being 100 at 0° C.
	Silver at 0° = 100.	Silver at 0° C. = 100.	Silver at 100° = 100.	
Silver	100	71·316	100	28·7
Copper	91·517	64·919	91·030	29·1
Gold...	64·960	48·489	67·992	25·4
Cadmium...	24·579	17·506	24·547	28·8
Zinc...	24·063	17·596	24·673	26·9
Tin	14·014	8·657	12·139	38·2
Iron...	12·350	8·387	11·760	32·1
Lead...	8·277	5·761	8·078	30·4
Platinum...	7·933	6·688	9·378	15·7
Mercury	1·7387	1·575	2·208	9·4

The measurement of electric conductivity may be attained more simply by the use of the instrument known as *Wheatstone's bridge*, combined with a single galvanometer of ordinary construction. This method is now extensively employed for the measurement of the conductivities of wires for telegraphic purposes (*Phil. Trans.* 1843, 323). The principle of the instrument will be understood with the aid of the following diagram :—

FIG. 230.



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Upon a slab of mahogany, *m m*, are fastened four stout copper wires, *c a*, *c b*, *z a*, *z b*, the extremities of which are attached to binding-screws. The binding-screws *z* and *c* are to be connected with the electrodes of a voltaic combination, *v*; the screws *a* and *b* are to be attached to the terminal wires of the galvanometer, *g*. Suppose, first, the four wires to be of equal length and thickness, and to be *continuous;* perfect equilibrium would in this case be established in the galvanometer, how powerful soever the current from the battery, and the needle would remain at zero: for the two currents, *z b g a c* and *z a g b c*, are exactly equal, and both tend to pass in opposite directions through the galvanometer; the tensions at *a* and *b* are equal, and the needle is consequently unaffected. But if a resistance be interposed in either of the four wires, the equilibrium of the needle is disturbed. Suppose, then, that the copper wire *c b* be divided at *e f*; the current from *c* will now pass entirely through the continuous wire *c a*; at *a* it will become divided, part passing through the wire *a z*, and a smaller portion through the galvanometer and the wire *b z*, which offers a greater resistance than the wire *a z* alone. If the interval at *e f* be completed by a conductor, such as a mile of copper wire of which the resistance is to be measured, a smaller amount of the current will traverse the wire *c e f b* than will pass along *c a*, and a proportionate amount of the current will pass through the galvanometer; but if now a resistance equal to that of the wire at *e f* be introduced at *h i*, the amount of electric tension at *a* and *b* will again become equalized, and the needle will remain stationary. By means of the resistance coils and rheostat, a known amount of resistance expressed in terms of the standard agreed upon, can be introduced at *h i*, and so the resistance of the wire at *e f* may be exactly determined in terms of this interposed resistance. Various modifications of the form of this apparatus may be used, and many precautions are needed to ensure the greatest attainable accuracy.

A modification of this method was applied by Matthiessen (*Phil. Mag.* 1857 [4], xiii. 81) in his researches upon the conductivities of wires of various metals (*Phil. Trans.* 1858, 383; 1862, 1; 1863, 369). He considers the metals in the first of the two following tables to have been chemically pure. The wires of the oxidizable metals were obtained by forcing them through an opening in a steel plate, by strong pressure, the wire as it was formed being received into a vessel filled with naphtha.

Matthiessen and Von Bose conclude from these experiments that the law of decrease of electric conductivity is the same for

Electric Conductivity of Metals. (*Matthiessen.*)

Metal (pure).	Conductivity. Silver at 0° C. = 100.		Conductivity at 100° C. Silver at 100° = 100.	Each metal compared with itself at 0° C. = 100.	
	At 0°.	At 100°.			Loss per ct.
Silver (hard-drawn) ...	100·00	71 56	100·00	71·56	28·44
Copper (hard-drawn) ...	99·95	70·27	98·20	70·31	29·69
Gold (hard-drawn)	77·96	55·90	78·11	71·70	28·30
Zinc (pressed)	29·02	20·67	28·89	71·23	28·77
Cadmium (pressed)	23·72	16·77	23·44	70·70	29·30
Palladium (annealed) ...	18·44				
Platinum (annealed) ...	18·03				
Cobalt	17·22				
Iron	16·81	10·38	14·50	61·74	38·26
Nickel	13·11				
Tin	12·36	8·67	12·12	70·11	29·89
Thallium	9·16	6·41	8·93	68·58	31·42
Lead	8·32	5·86	8·18	70·39	29·61
Arsenic	4·76	3·33	4·65	69·88	30·12
Antimony	4·62	3·26	4·55	70·54	29·46
Bismuth	1·245	0·878	1·227	70·51	29·49

all metals, and it will be at once apparent that the relative conductivities of the metals continue to be the same with trifling variation, whether they be compared at 0° or at 100° C., as will be evident by comparing the first and third columns of figures with each other. The numbers given for palladium, platinum, cobalt, iron, and nickel are calculated as on pure specimens from experiments upon specimens of these metals known to be slightly impure. In the table which follows, the metals were commercially pure, but the conductivity, when not absolutely accurate, is probably below the truth, as the addition of a second metal always diminishes the conductivity.

Metal.	Conductivity.	Temp. ° C.	Temp. ° F.	Metal.	Conductivity.	Temp. ° C.	Temp. ° F.
Silver (pure)	100·00	0·0	32·0	Iron	14·44	20·4	68·7
Copper	77·43	18 8	65·8	Palladium ...	12·64	17·2	63·0
Sodium ...	37·43	21·7	71·0	Platinum	10·53	20·7	69·3
Aluminium ...	33·76	19·6	67·2	Strontium ...	6·71	20·0	68·0
Magnesium ...	25·47	17·0	62·6	Mercury	1·63	22·8	73·0
Calcium ...	22·14	16·8	62·2	Tellurium ...	·000777	19·6	67·3
Potassium ...	20·85	20·4	68·7	Red Phosphorus	·00000123	20·0	68·0
Lithium ...	19·00	20·0	68·0				

Matthiessen finds that scrupulous attention to the purity of the metals is essential. The presence of 2·5 per cent. of phosphorus in copper reduced the conductivity of a specimen of the pure metal from 100 to 7·78. A mere trace of arsenic in the copper reduced it from 100 to 60, and the presence of a little suboxide

in the metal had a very marked effect in reducing the conductivity (Matthiessen and Holzmann, *Phil. Trans.* 1860, 85). Indeed, there are few metals more easily affected in conductivity by slight traces of impurity than copper, so that very great differences in conductivity are observed in wires drawn from different samples of what would be regarded as good commercial copper.

The conductivity of an alloy is generally below that of the mean of its component metals. This is seen in the alloy of antimony and tin; but the alloys of tin and lead, tin and zinc, zinc and cadmium, give a conductivity almost exactly the mean of those of the component metals, allowing for the proportion of each that is present (Matthiessen, *Phil. Trans.* 1860, 161). A similar fact was observed by Calvert and Johnson (149) in the conductivity for heat of some of these very alloys. An elaborate paper on the influence of temperature on the conductivity of alloys, by Matthiessen and Vogt, will be found in the *Phil. Trans.* for 1864, 167.

Alloy.	Silver = 100.		Temperatnre.	
	Calculated Conductivity.	Observed Conductivity.	° C.	° F.
ZnCd	24·04	23·78	20·8	69·4
ZnSn	17·13	17·43	22·0	71·6
Sn_4Pb	10·31	10·55	22 0	71·6
SnPb	9·09	9·20	21·4	70·5
$SnPb_4$	8·22	8·26	22·6	72·7
2 Antimony, 1 part tin	11·99	0·413	25·0	77·0

Lenz found that all the metals continued to decrease in conductivity as the temperature rose to 200° C., and Dr. Robinson proved that this diminution continued as they were raised progressively to a red and even to a white heat.

The non-metallic bodies appear to increase in conductivity as the temperature rises, for Matthiessen found that the conductivity of graphite and of coke was increased by heating them, that of gas coke rising about 12 per cent. between the ordinary atmospheric temperature and a 'light' red heat. Hittorf obtained an analogous result with selenium. Comparing the conductivity at ordinary temperatures of different forms of carbon with that of silver at 0° C. as 100, Matthiessen obtained the following values:—

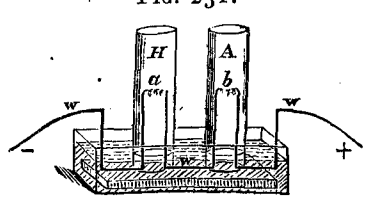
	° F.	° C.
Brodie's purified Ceylon graphite	0·0693 at 71 6	22
Gas coke	0·0386 at 77	25
Bunsen's battery coke	0·0246 at 79·2	26·2

(277) If equal quantities of electricity, whether obtained from the voltaic battery or from the electrical machine, be made to traverse wires of different metals of equal length and diameter in the same interval of time, the rise of temperature in the wire is inversely proportional to its conductivity, and therefore the better the conductor the less heat does it emit. The general truth of the fact may in the case of voltaic electricity be rudely but strikingly demonstrated by taking a wire of silver and one of platinum, each of exactly the same diameter, and forming them into a compound wire consisting of alternate links of the two metals. A current of electricity may be transmitted through this compound wire, of such a strength as to heat the platinum to visible redness, whilst the silver links will exhibit no such intense heat, though each link of the wire, from the form of the experiment, must transmit equal quantities of electricity in equal times. It has been ascertained that the heat developed at any part of the circuit is proportional to the square of the current multiplied into the resistance at that particular point. For the same wire the rise of temperature is proportioned to the square of the current, and this is true also for liquid conductors.

Andrews (*Proceed. Roy. Irish Acad.* 1841, 465), found that when a fine platinum wire was traversed by a current from one of Daniell's constant batteries, the ignition of the wire varied in intensity by varying the gas with which he surrounded the wire. This wire was enclosed in a glass tube, which could be filled at pleasure with the different gases in succession. It was found that gaseous sulphurous anhydride and hydrochloric acid had a smaller cooling power than atmospheric air. Nitrogen, carbonic oxide, cyanogen, carbonic anhydride, nitric oxide, nitrous oxide, oxygen, and aqueous vapour, had nearly the same effect as atmospheric air. Olefiant gas, ammonia, the vapour of alcohol and of ether had a greater cooling power; and hydrogen a far greater cooling power than any of the others. The same subject has also been investigated by Grove (*Phil. Trans.* 1849, 49).

The following experiment illustrates the cooling power of hydrogen very clearly. Take three pieces of stout copper wire, bend them into the form shown at w w w, fig. 231, and attach them to a weighted board, by which the lower part of the bends can be sunk beneath the surface of water contained in a shallow vessel. At

Fig. 231.



a and *b*, where the wires project above the surface of the water, complete the connexion by means of spirals of fine platinum wire, both spirals being equal in length, and each cut from the same wire. Each spiral will thus oppose an equal resistance to the passage of the current. When a voltaic current of a certain strength is transmitted through the wire, w w w, each spiral, consequently, becomes heated to the same degree of visible ignition. But if two similar jars, one, A, filled with air, the other, H, filled with hydrogen, be inverted over them, the wire in the jar H immediately ceases to be luminous, while that in A becomes more intensely ignited. This superior cooling power of the hydrogen is no doubt mainly due to the superior mobility of the particles of the gas over those of air (152, 160).

The experiment was varied by enclosing the wires *a* and *b* in separate glass tubes, and sealing them up, one in an atmosphere of air, the other in an atmosphere of hydrogen. Both were then included in the same circuit, so that they should transmit equal currents of electricity. Before transmitting the current, however, each tube was immersed in a separate vessel which contained a given quantity of water, the temperature of which was accurately observed. After the current had been allowed to pass for a certain time, the temperature of the water which surrounded each wire was again observed, and it was found that the water around the tube which contained air was considerably hotter than that surrounding the tube filled with hydrogen.

This result, paradoxical as it appears, and as it seems to have been regarded by Grove, must necessarily follow from the operation of two principles which have already been explained: the first of these is, that the resistance offered by a metal to the passage of electricity is diminished by reducing the temperature; and the second is that the heat evolved by a current in passing through a conductor is inversely as the resistance which it experiences. Now, in this experiment, the primary effect of the hydrogen is the cooling of the conducting wire; and the consequence is that this cooled wire, in transmitting the same current as a similar wire in air, offers less resistance, and less heat is therefore evolved by the wire surrounded by the hydrogen than by the wire which is surrounded by air.

(278) *Electric Conductivity of Liquids.*—Liquids are very inferior to solids in conductivity; indeed, the difference between the two classes of bodies is so extreme that it is difficult to institute an accurate comparison between them. The attempt, however, has been made by Pouillet (*Comptes Rendus*, 1837, iv.

785): assuming as the unit of comparison the conductivity of a solution of cupric sulphate, saturated at 15° C. he gives the following as the relative conductivity of the undermentioned solutions:—

Saturated solution of cupric sulphate . .	1
Ditto, diluted with an equal bulk of water .	0·64
Ditto, diluted with twice its bulk of water .	6·44
Ditto, diluted with four times its bulk . .	0·31
Distilled water	0·0025
Ditto, with $\frac{1}{200}$ of nitric acid	0·015
Platinum wire	2,500,000·00

The conductivity of a platinum wire, of a diameter and length equal to that of the interposed columns of liquid, is probably estimated too high.

Since these results of Pouillet's were published, the subject of the conductivities of liquids has been resumed by E. Becquerel (*Ann. de Chimie*, 1846 [3], xvii. 242). He states that saline solutions may be divided into two classes; in the first, the conductivity increases progressively in proportion to the strength of the solution, until it becomes saturated; cupric sulphate and sodic chloride affording instances of this kind: whilst in the second class, of which cupric nitrate and zincic sulphate may be taken as examples, the conductivity increases with the degree of concentration up to a certain point, beyond which it diminishes as the solution becomes more nearly saturated. The salts which exhibit this peculiarity are either deliquescent or extremely soluble. The table on p. 564 contains a few of Becquerel's results. The saline liquids are to be considered as saturated unless otherwise specified.

It is not surprising that differences so considerable should be observed between the conductivities of liquids and those of solids; for the processes of conduction in the two cases are essentially different. In liquids chemical decomposition and free movement of the component particles are indispensable, whilst nothing of the kind takes place in solids. The effects of heat are even inverted in the two cases; for experiment shows that as the temperature rises, the conductivity of the liquid increases rapidly; according to Becquerel, the conductivity of many solutions at 100° C. is three or four times as great as that of the same solution at 0°. These phenomena, therefore, are the reverse of those presented by most solids. Exceptions, however, occur: Faraday has shown that argentic sulphide, when cold, is an

insulator, but on warming it gently it begins to conduct, and when hot it affords a spark like a metal; at a point a little below redness it conducts sufficiently to maintain its conductivity by the heat produced by the current which it transmits. Plumbic sulphide and fluoride, as well as mercuric iodide, also exhibit the same peculiarity. Glass, when cold, is an excellent insulator of the electricity developed by friction, but when heated it conducts, and when red hot it possesses scarcely any insulation; the same thing is also true of the tourmaline. Gutta percha is a much better insulator at 0° C. than at 40°, and the same thing is observed, though to a much less extent, in the case of caoutchouc. Most of these cases have been traced to a partial chemical decomposition of the compound under the influence of softening by heat (Beetz, *Phil. Mag.* 1854 [4], viii. 191). When liquefied by heat, these compounds nearly all undergo chemical decomposition, and allow the current to pass freely.

Electric Conductivity of Liquids.

Substances used.	Density.	Temp. °C.	Temp. °F.	Conductivity.
Pure Silver...		0	32	100,000,000·00
Solution of Cupric Sulphate ...	1·1707	9·25	48·6	5·42
Do. half the strength... ...		,,	,,	3·47
Do. one fourth the strength		,,	,,	2·08
Solution of Sodic Chloride... ...		13·4	56·1	31·52
Do. half the strength... ...		,,	,,	23·08
Do. one fourth the strength		,,	,,	13·58
Solution of Cupric Nitrate... ...	1·6008	13·0	55·4	8·995
Do. half the strength... ...		,,	,,	17·073
Do. one fourth the strength		,,	,,	13·442
Solution of Zincic Sulphate ...	1·4410	14·4	57·9	5·77
Do. half the strength... ...		,,	,,	7·13
Do. one fourth the strength		,,	,,	5·43
Oil of Vitriol 1 measure ... } Distilled Water 11 measures }		19·0	66·2	88·68
Nitric Acid (Commercial)	1·31	13·1	55 6	93·77
Platinum		0·0	32	7,933,000·00

(279) *Electric Conductivity of Gases.*—Gases are almost perfect insulators of the voltaic current; although some feeble indications of conductivity have been discovered by Andrews, as well as by Hankel, by E. Becquerel, and by Buff, in a highly rarefied atmosphere, between metallic surfaces strongly ignited and in close approximation; and Magnus finds that small as is the conductivity of gases, they differ in degree in this respect, hydrogen surpassing other gases and vapours.

Grove has further shown (*Phil. Mag.* 1854 [4], vii. 47) that

in flame a current of electricity is not only transmitted, but that there is evidence of its production within the flame, and he attributes its origin to chemical action. Becquerel regards this as a thermo-electric phenomenon (*Ann. de Chimie*, 1854 [3], xlii. 411). Becquerel's experiments, however, are not conclusive; and the feebleness of thermo-electric currents, coupled with the slight conductivity of flame, render such a view inadmissible. If two platinum wires be connected with the extremities of a galvanometer, the free ends of the platinum being twisted into a small coil, and one of the platinum wires be inserted into the root of the blowpipe flame, whilst the other is introduced just in front of the apex of the blue cone, a current will be indicated, passing from the root to the apex of the flame. By forming several jets of flame together into a compound circuit, Grove succeeded in decomposing a solution of potassic iodide by means of the currents obtained from flame. Under certain circumstances, however, which we now proceed to notice, highly heated gaseous matter appears to transmit voltaic electricity of high intensity, and the phenomena thus displayed are of a most brilliant and remarkable kind.

(280) *Disruptive Discharge—Electric Light.*—When the current is greater than the conductor is able to convey, the wire melts, and is dispersed in vapour; disruptive discharge, in fact, occurs. From a powerful voltaic battery this disruptive discharge may be maintained continuously, owing to the enormous quantity of electricity in circulation.

If the air be rarefied between the interrupted conductors, the interval through which the discharge can be effected may be considerably increased. The heat developed by the passage of the current between two pieces of charcoal when they are in contact, will enable them to be separated for a considerable distance without interrupting the passage of the current; this distance ranges from $18^{mm.}$ to $25^{mm.}$ when a series of seventy of Daniell's cells 50 centim. in height are employed. Davy, with the great battery of the Royal Institution, consisting of 2000 pairs of plates on Wollaston's construction, obtained an arc of flame, between charcoal points, 4 inches (10 centim.) in length, and of dazzling brilliancy.

Despretz, by using 600 cells of Bunsen's construction arranged consecutively, succeeded when the points were placed in a vertical line with the negative pole below, in obtaining an arc $183^{mm.}{\cdot}5$ (about 7·2 inches) in length. With 100 pairs the arc was only

$25^{mm}\cdot 2$ long. The most intense light, however, is obtained when the points are separated but to a small distance, because the resistance then being less, a much larger quantity of electricity passes in a given time, and the temperature is proportionately higher. Despretz found he obtained a much more intense light by employing his 600 cells in six parallel series so as to form 100 cells of six times the ordinary size, than when they were connected into one continuous series. He estimated the light with the arrangement of 600 in six parallel series to be nearly six times as great as when 100 cells only were employed,—a result in conformity with the anticipations of theory. The same observer found that when the charcoal points were disposed in a horizontal direction at right angles to the magnetic meridian, the length of the arc when 200 pairs of Bunsen in two parallel series were employed, was greater in the proportion of 20·8 to 16·5, when the positive pole was to the east than when it was to the west (*Comptes Rendus*, 1850, xxx. 370).

During the production of this dazzling light a considerable mechanical transport of the materials composing the terminals of the pile takes place, and there can be no doubt that the ignition of the solid particles contributes mainly to the production of the intense light thus procured. A cavity is always produced in the piece of charcoal attached to the positive wire which is connected with the last platinum or copper plate of the battery; and at the same time a mammillated deposit, which continually increases in length, is formed upon the charcoal on the negative wire in connexion with the zinc plate; and usually portions of the charcoal become converted into glistening plates of true graphite. Attempts have been made to apply the electric light to the purposes of illumination, and in particular cases, as for temporary application to illuminating works in process of construction at night, or for the display of optical phenomena in the class-room, it is often of high value. Its application is, however, attended with great practical difficulties, of which the transfer of conducting-material from one pole to the other is one of the most serious; and it is very doubtful if, even when the mechanical obstacles are removed, such a light can be economically or advantageously used for the general purposes of illumination. The light is too intense for the unprotected eye to endure for any length of time in its immediate vicinity, and the expense is so great, that unless the electricity can be obtained in the process of preparing some chemical compound in the battery itself which will defray the cost

of production, its success as a mercantile speculation is very problematical.* According to E. Becquerel, the cost of the electric light is nearly four times as great as that of an equal light produced by burning coal gas.

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* The general appearance of the electric lamp of Duboscq is shown in fig. 232, in which T, T represent the charcoal points between which the voltaic arc is maintained. The object to be effected is to preserve these points at a uniform distance from each other, and at the same height in the lantern, so that the source of light shall always be kept in the same position with respect to the lens.

The regulator by which this result is attained is shown at R. Within this is an electro-magnet, and a clock movement, the principal parts of which are represented upon a larger scale in fig. 233. The clock movement is designed to

FIG. 232.

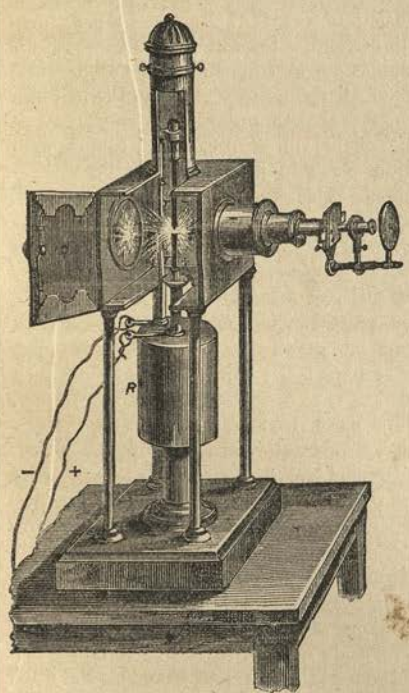
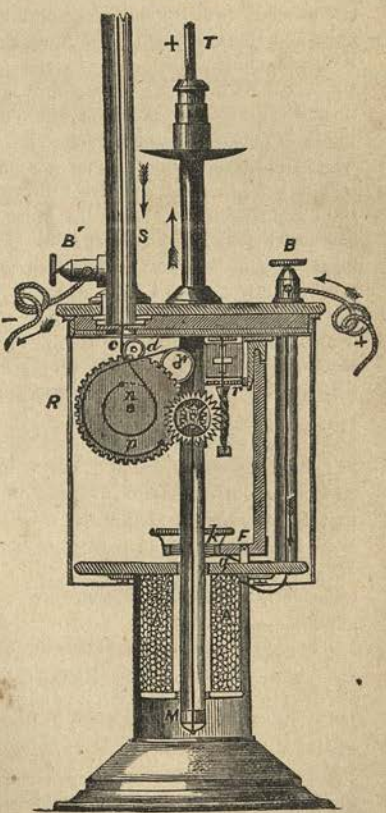


FIG. 233.



bring the two points towards each other so as to compensate for the waste they experience in burning, and the electro-magnet is employed to check the clock

This transfer of solid particles is not confined to cases in which a porous conductor like charcoal is used. The densest metals, such as platinum and iridium, are transferred from the positive towards the negative terminal, but the arc in these cases is not so long as when more friable materials are used. When

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action when no longer needed. When the battery is in use the negative point is always consumed in air more slowly than the positive one; and it becomes necessary to provide means for moving each point, at a rate proportioned to the rapidity of its consumption. This is effected by making the drums *n* and *p* of unequal dimensions; the chains *c* and *d* are employed to transmit the movement of the clockwork to the points T, T′. The chain *c* attached to the upper or negative point T′, is coiled upon the smaller drum *n*, and passes up the tubular support *s*. This chain is wound in the opposite direction to that of the chain *d*, which after passing over the pulley *d′*, is attached to the tube containing the lower or positive charcoal point T. Both drums are placed upon a common axis, and therefore both are moved by the clock in the same direction, so that whilst the chain *d* attached to the lower point is being wound up, the chain *c* connected with the negative point is being unwound, though less rapidly than *d*, and the negative point is allowed to descend. Instead of chains, which are liable to get out of order, racks and pinions are now generally employed. The wires from the battery (about 40 pairs of Grove) are made fast to the binding-screws B B′, the positive wire B being connected with one end of the coil A A of the electro-magnet M, while the other end of this coil is in electrical contact with the lower point T. The current is thus made to pass through the electro-magnet on its way to the charcoal points. When the electro-magnet is in full action it attracts the keeper *k* attached to the lower end of the bent lever working on the fulcrum F. The upper extremity of this lever, when the keeper is drawn home, locks into the ratchet wheel seen edgewise at *r*; thus arresting the clock movement, and rendering the charcoal points stationary. As soon as the distance between the points becomes too great, the current through the electro-magnet becomes reduced in strength, and lets go the keeper *k*, which is forced away from the magnet by the releasing spring *q*. By this means the clockwork is immediately set free, and the points are thus made to approach each other, until the current recovers sufficient force again to attract the keeper, which once more locks into the ratchet wheel *r*. When the battery is in good action, these alternate motions of the keeper and of the clockwork recur with frequency and regularity; so that the points are maintained at a distance sufficiently constant to prevent any sudden or material fluctuation in the amount of light.

Duboscq has also constructed a lamp with two trains of clockwork, one causing the carbon points to approach and the other separating them. When the points are at the proper distance from one another, an electro-magnet checks both trains, if the current is too weak the train which brings the points together is started; if, on the contrary, the current passing is too powerful, the other train is set in motion. This arrangement prevents the possibility of the carbon points coming in contact, which sometimes happens with the other form of lamp.

Mr. Browning has devised a lamp in which the points are kept in contact by gravity, but on passing the current, an electro-magnet is brought into action, which maintains the points at the required distance from one another.

a positive coke point was opposed to a negative electrode of platinum, the arc was not more than half the length of that obtained by making the coke negative and the platinum positive (De la Rive). Grove found it to be true generally that in an oxidizing medium the brilliancy and length of the arc was greatest with the most oxidizable metals. Van Breda states that portions of the negative terminal are always transferred towards the positive wire. This was particularly evident when iron balls were made the terminals of the wires, although this transfer is much less in amount from the negative to the positive, than the simultaneous transfer from the positive to the negative wire. The light that attends the voltaic arc does not necessarily proceed from the combustion of the conducting material, for it occurs in a vessel from which air is exhausted, with a brilliancy not much inferior to that exhibited by it in the air. It may even be produced between two charcoal points which are immersed under water. In every case, however, the transference of some material particles is essential to the production of the luminous arc. Gassiot found that even when a combination of 320 cells on Daniell's construction was employed, no spark could be obtained between two platinum surfaces, connected one with one wire, the other with the opposite wire of the battery, in a high state of efficiency, although the two platinum surfaces were brought within $\frac{1}{3000}$ of an inch ($0{\cdot}0084^{mm.}$) of each other. If, however, the transfer of some material particles be effected between the two surfaces, either by a momentary contact, or even by the discharge of a Leyden jar across the interval, the current may be established and the luminous arc maintained with a small number of pairs of plates. By very much increasing the number of pairs, Gassiot succeeded in raising the tension to such an extent that the spark would spring across the interval between the terminals of the battery wires. Mr. Warren De La Rue, with his battery consisting of 8040 cells, has obtained sparks in air, between a point positively and a disk negatively charged, of the length of $8^{mm.}{\cdot}5$ (·348 inch.) (299).

The heat produced in the voltaic arc is of the most intense kind. Metals like platinum, iridium, and titanium, which resist the greatest heat that can be obtained by the direct chemical action attendant upon combustion in the furnace, melt readily, and are transferred from the positive to the negative terminal by a voltaic current of high intensity. The fusion is easily accomplished by excavating a circular piece of gas coke, about an inch ($25^{mm.}$) in diameter and half an inch ($12^{mm.}$) thick, into the form of a crucible, which is attached by stout copper bell-wire to the

wire which is in connexion with the last platinum plate of the battery; a piece of boxwood charcoal or of gas coke about the thickness of a cedar pencil is attached to the wire connected with the zinc plate of the battery; the metal for trial is then placed in the little coke crucible, and the current from 20 or 30 pairs of Grove's battery is transmitted through it by means of the charcoal point with which the negative wire of the battery is armed. Alumina, rutile, oxide of iron, and other refractory bodies, may be fused in the voltaic arc, and subsequently volatilized. Despretz, with his powerful battery of 600 cells, in six parallel series of 100 each, saw charcoal obtained from anthracite, from graphite, from sugar, and from oil of turpentin, when moulded into the form of rods, and heated in an atmosphere of nitrogen under a pressure of between 2 and 3 atmospheres, soften, bend, and swell up: in some cases he cemented together the softened fragments into one mass, and the interior of the vessel was lined with a black deposit of what he supposed to have been volatilized carbon. Gassiot has pointed out the remarkable fact, of which no explanation has as yet been given, that the positive wire, or the wire connected with the terminal platinum plate of the battery, becomes much the hotter of the two in this action. This effect is reversed in the case of the secondary current obtained from the Ruhmkorff coil (312), in which the negative terminal becomes the hottest, and from which the dispersion of solid particles almost exclusively occurs.

Favre (*Ann. de Chimie*, 1854 [3], xl. 293) has arrived at the interesting conclusion that the quantity of heat evolved by the solution of a definite quantity of zinc in any given circuit is lessened in the battery itself, in proportion as heat is evolved at any given point of the circuit, and that heat is lost when motion is produced by the development and exertion of electro-magnetic power. The quantity of heat thus lost agrees very closely with the quantity required by theory if Joule's mechanical equivalent of heat (129) be adopted. A part of the heat is thus converted into mechanical work, as must be the case if the mechanical theory of heat (130) be true. The simple solution of a given quantity of zinc in sulphuric acid, equal in amount to that dissolved in the battery during each experiment, has been found by previous researches to be represented by the number 18682. In these experiments Favre arranged the battery itself in a calorimeter; and in a second calorimeter he placed the conducting wire, which was coiled in such a manner as to be applicable to the production of electro-magnetic action, the amount of which could be measured by its power of raising a weight. He then

made five series of experiments. In the first of these the current traversed the battery only and a short copper wire; in the second series, it traversed the battery and the conducting wire of the coil, the iron not being included in the coil; in the third series, the metallic core was previously placed in the axis of the coil; in the fourth series, the apparatus for rotation was set in motion by the electro-magnetism developed, but no weight was raised; and in the fifth series, a known weight was lifted to a definite height by the action of the electro-magnet. The results were as follows:—

No. of Experiments.	1st. Calorimeter. (Battery.)	2nd Calorimeter. (Conducting coil.)	Heat lost for Weight raised.	Heat Units. Total.
1	18682			18682
2	18674			18674
3	16448	2219		18667
4	13888	4769		18657
5	15427	2947	308	18682

The fifth column gives the total amount of heat measured in 'units of heat' (see p. 284), from which it will be seen to be sensibly equal in each case.

The colour of the light emitted by the different metals when deflagrated between the wires of the battery, is peculiar for each: gold produces a bluish-white light, silver a beautiful green light, copper a reddish white, mercury a brilliant white light tinged with blue; steel burns with brilliant yellow scintillations, zinc with a powerful white light tinged with blue, and lead with a purple light. If these lights be viewed separately through a glass prism, large dark intervals will be seen between a few brilliant streaks of light of different colours and of definite degrees of refrangibility, so that each metal may be recognised by the spectrum that it gives in the voltaic arc (107, 108).

Chemical Actions of the Voltaic Battery.

(281) *Discharge by Convection.*—To the chemist, however, the discharge of the voltaic current by the process of convection, is even more interesting than the brilliant phenomena exhibited by the disruptive discharge, since it is in the discharge by convection that the important chemical actions of electricity are displayed.

It has already been explained when describing the voltameter (272), that if the connecting wires of a voltaic battery terminate in platinum plates or wires which are made to dip into acidulated water, decomposition of the liquid takes place, oxygen being

evolved at the surface of one of the platinum plates, while hydrogen escapes at the surface of the other. This important discovery was made in the year 1800, by Nicholson and Carlisle, and the chemical action of the voltaic pile thus revealed, enabled Davy a few years later to decompose the alkalies and earths, which up to that time had been regarded as elements; but by showing their compound nature he at once modified, in an important manner, the views of chemical philosophy which had prevailed up to that period.

In pursuing these experiments on the voltaic decomposition of water, it was soon observed that when copper wires, or the wires of metals which are easily susceptible of oxidation, are employed, gas escapes from one wire only; whilst if platinum or gold wires be used, gas is evolved from both. In the first case, the oxygen combines with the copper or oxidizable metal, and forms an oxide which is dissolved by the acid liquid, and therefore hydrogen alone escapes; in the second case, both gases are evolved, one from either plate; since neither platinum nor gold has sufficient chemical attraction for oxygen to combine with it at the moment of its liberation.

The process of resolving compounds into their constituents by electricity, is termed *electrolysis* (from 'electricity' and λύσις, releasing); a body susceptible of such decomposition is called an *electrolyte;* and the terminating wires or plates of the battery are called the *poles* of the battery. The word *electrode* is also used as synonymous with the pole of the battery, and it implies the door or path (from ὁδός, a way) to the current by which it enters or leaves the compound through which it is transmitted. The wires connecting the electrodes with the battery were termed by Ampère *rheophores* (from ῥέος, a stream, and φορέω, I carry).

(282) *Laws of Electrolysis.*—A great variety of bodies admit of being decomposed by electrolysis, but the process is not applicable to all indiscriminately. It occurs under certain definite laws, which may be stated as follows:—

i. *No elementary substance can be an electrolyte:* for from the nature of the operation, compounds alone are susceptible of electrolysis.

ii. *Electrolysis occurs only whilst the body is in the liquid state.* The free mobility of the particles which form the body undergoing decomposition is a necessary condition of electrolysis, since the operation is always attended by a transfer of the component particles of the electrolyte in opposite directions. Electrolysis is necessarily a process of electrical conduction, but it is conduction

of a peculiar kind; it is totally different from that of ordinary conduction in solids. If an electrolyte be solidified, it instantly arrests the passage of the current; for it cannot transmit the electric current like a wire or a solid conductor: the thinnest film of any solidified electrolyte between the two electrodes suspends all decomposition. Many saline bodies are good conductors when in a fused condition; for example, nitre whilst in a fused state conducts admirably; but if a cold electrode be plunged into the melted salt, it becomes covered with a film of solid nitre, and no current is transmitted until a continuous chain of liquid particles is restored between the plates by the melting of the film; these effects are readily exhibited by including a galvanometer in the circuit. A few partial exceptions to this rule have been observed, and have already been alluded to (278); but in such cases the decomposition is always extremely limited.

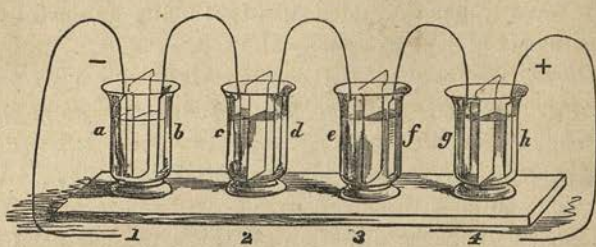
iii. *During electrolysis, the components of the electrolyte are resolved into two groups: one group takes a definite direction towards one of the electrodes; the other group takes a course towards the other electrode.* This direction of the *ions* (as the two groups which compose the electrolyte have been termed, from ἰών going) depends upon the direction in which the chemical actions are going on in the battery itself. The two platinum plates in the decomposing cell may be distinguished from each other in the manner proposed by Daniell. These plates occupy respectively the position of a zinc and of a platinum plate in an ordinary cell of the battery: that is to say, if for this decomposing cell an ordinary battery cell were substituted, a rod of zinc would occupy the place of one of the platinum plates, and would be attacked by the oxygen and acid in the exciting liquid of the battery, whilst a plate of platinum or some other conducting metal would occupy the place of the second platinum plate, and would have the hydrogen of the exciting liquid directed towards it. To the plate of the decomposing cell which corresponds to the zinc rod, Daniell gave the name of the *zincode*, which is synonymous with the *anode* of Faraday and the *positive pole* of other writers. To the plate which corresponds to the platinum or conducting metal, Daniell gave the name of the *platinode*, which is synonymous with Faraday's term of *cathode*, and with the *negative pole* of other writers. Oxygen, chlorine, and the acids generally, make their appearance at the zincode in the decomposing cell during electrolysis; whilst hydrogen, alkalies, and the metals are evolved upon the platinode.

This definite direction which the elements assume during

electrolysis may be shown by collecting the gas which is evolved over two platinum plates, connected, one with the last platinum, the other with the last zinc plate, of a combination consisting of three or four pairs of Grove's battery. Hydrogen will be collected over the platinode, or the plate in connexion with the zinc end of the arrangement; whilst from the zincode, or plate in connexion with the terminal platinum plate of the battery, oxygen is evolved.

The following experiment further illustrates the definite direction which the components of the electrolyte assume. Let four glasses be placed side by side, as represented in fig. 234, each

FIG. 234.

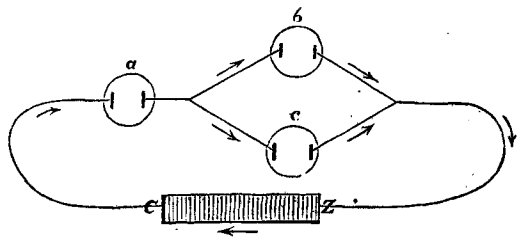


divided into two compartments by a partition of card, or three or four folds of blotting-paper, and let the glasses be in electrical communication with each other by means of platinum wires which terminate in strips of platinum foil. Place in the glass No. 1, a solution of potassic iodide mixed with starch; in 2, a strong solution of common salt, coloured blue with sulphate of indigo; in 3, a solution of ammonic sulphate, coloured blue with a neutral infusion of the red cabbage; and in 4, a solution of cupric sulphate. Let the plate, *h*, be connected with the positive wire, and let *a* complete the circuit through the negative wire. Under these circumstances iodine will speedily be set free in *b*, and will form the blue iodide of starch; chlorine will show itself in *d*, and will bleach the blue liquid; sulphuric acid will be seen in *f*, and will redden the infusion of cabbage; sulphuric acid will also be liberated in *h*, as may be seen by introducing a piece of blue litmus paper, which will immediately be reddened; whilst a piece of turmeric paper will be turned brown in *a*, from liberated potash; in *c* it will also be turned brown by the soda set free; in *e* the blue infusion of cabbage will become green from the ammonia which is disengaged; and in *g* metallic copper will be deposited on the platinum foil.

iv. *The amount as well as the direction of electrolysis is definite, and it is dependent upon the action in the battery; being directly proportionate to the quantity of electricity in circulation.* It has been amply proved by experiment that for every 65 milligrammes of zinc which is dissolved in any one cell of the battery, provided local action be prevented, 18 milligrammes of water are decomposed in the voltameter; or if, as in the preceding experiment, several electrolytes be arranged in succession, each compound will experience a decomposition proportioned to its chemical equivalent. For instance—if the current be made to pass first through fused plumbic iodide (PbI_2), and then through fused stannous chloride ($SnCl_2$)—for each 65 milligrammes of zinc dissolved in any one cell of the battery, 207 milligrammes of lead, and 118 milligrammes of tin will be separated on the respective platinodes, whilst 254 (or 2×127) milligrammes of iodine, and 71 milligrammes or $2 \times 35{\cdot}5$ milligrammes of chlorine will be evolved on the respective zincodes. These numbers correspond with the chemical equivalents (not the atomic weights) of the several elements named.

Variations in the intensity of the current (*i.e.*, variations in the quantity of electricity which passes through a given transverse section of the conductor in unit time) produce no variation in the amount of chemical decomposition which is effected by the arrangement. For example: if three similar voltameters, provided with plates of equal area, be arranged as at *a*, *b*, *c*, fig. 235, the first will transmit twice as much electricity in a given time as either of the others. The current will therefore have twice the intensity in *a*; but the total quantity of gas collected from *b* and *c* together will be exactly equal to the total amount yielded by *a* in the course of the experiment. Hence it follows that the quantity of electricity which is separated from a given quantity of matter in the act of combination is able, irrespective of its intensity, when thrown into the current form, to produce the decomposition of an *equivalent quantity* of any compound body which is susceptible of electrolysis; and hence it has been concluded that the equivalent weights of the simple bodies are those weights of

FIG. 235.



each substance which are associated with equal quantities of electricity, and have naturally equal electric powers.

To these laws may be added a fifth—viz.:

v. *Those bodies only are electrolytes which are composed of a conductor and a non-conductor.* The conductors accumulate on the platinode, the non-conductors on the zincode. For example, plumbic iodide when melted conducts the current; metallic lead, which is a conductor, accumulates at the platinode; whilst iodine, which is a non-conductor even when melted, collects at the zincode. On the other hand, red chloride of sulphur ($S''Cl_2$) is not an electrolyte, although composed of single *equivalents* of its components; and melted sulphur, and chlorine, when the latter is liquefied by pressure, are both insulators of electricity. A compound composed of two conductors is equally unfit for electrolysis. For instance, a metallic alloy, such as plumber's solder, composed of two parts, or one equivalent, of lead, and one part, or one equivalent, of tin, when melted, conducts the current perfectly, but no separation of its constituents is effected.

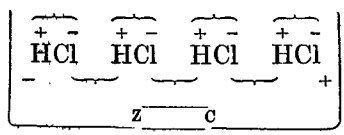
(283) *Relative Decomposability of Electrolytes.*—Every electrolyte, since it can transmit a current, is also capable of generating a current if it be employed to excite action in the battery itself. Comparatively few electrolytes, however, are practically available for this purpose. It is necessary that the deposited compounds be dissolved as fast as they are produced; otherwise the crust of insoluble matter which is formed upon the plates of the battery introduces a mechanical obstacle by which the action is speedily checked.

Great differences occur in the facility with which different electrolytes yield to the decomposing power of the voltaic current. Generally speaking, the greater the chemical opposition between the elements of a compound the more readily it yields to electrolysis. The following table exhibits the order in which, according to Faraday, the different compounds which are enumerated yield to electrolysis; those which are most readily decomposed standing first on the list:—

Solution of potassic iodide	Fused plumbic iodide
Fused argentic chloride	Hydrochloric acid
Fused zincic chloride	Diluted sulphuric acid.
Fused plumbic chloride	

(284) *Electro-chemical Actions.*—The suspension of chemical action which occurs under the influence of electrical induction is

one of the most interesting illustrations of the correlation of physical forces. This suspension is well shown in the way in which zinc when placed in contact with copper beneath the surface of sea-water, acts in preventing the corrosion of copper, and transfers to itself the chemical energy which would otherwise be manifested upon the copper (261). A similar suspension of chemical action is produced in the ordinary case of the decomposition of water between two platinum electrodes by the voltaic current; here the electricity appears to act by weakening, or rather by partly neutralizing, ordinary chemical attraction in one direction, whilst it strengthens or adds to it in the opposite, and hence the particles which were previously in combination with each other lose their attraction one for the other, and acquire it for those particles which are next adjacent to them in the liquid; if, for instance, the brackets above the subjoined formulæ indicate the state of combination of the elements of hydrochloric acid before the passage of the current, the brackets below would indicate the effect produced after its transmission, thus:—



Here z c is supposed to represent the battery, and + and − the terminal wires of the arrangement: the positive electricity seems to detach the chlorine adjacent to it from the hydrogen with which it was previously in combination, whilst the negative electricity produces a similar effect upon the contiguous particles of hydrogen, and the intermediate portions are polarized in the manner above represented.

The following modification of this experiment also shows in a striking manner the remarkable influence of electric polarity upon chemical attraction:—If two separate glasses filled with diluted sulphuric acid be placed side by side, and into one glass the negative wire of the battery is plunged, whilst the positive wire dips into the other cell, no decomposition will ensue; but if a connexion be established between the two glasses by means of a slip of platinum foil, one end of which is made to dip into each, the current will be immediately transmitted: hydrogen will be evolved upon the platinode in one glass, and oxygen upon the zincode in the other glass; whilst owing to the polar condition into which the connecting slip of platinum is thrown, hydrogen will be given off from one end of the slip, and oxygen will be

evolved upon the other extremity of it, although the metal itself experiences no sensible change beyond a slight rise of temperature.

(285) *Electrolysis of Salts.*—It has already been stated (282, iv.) that when a binary compound, such as a fused chloride or an iodide, is submitted to electrolysis, the ions or components of the compound are separated at the respective electrodes in equivalent proportions; the metal appearing at the platinode, whilst the chlorine, or corresponding element, is deposited at the zincode. If the zincode of the battery be formed of a substance capable of combining with the chlorine or corresponding element, an equivalent amount of the chloride or other compound of this metal will be formed there; and when the metal of the zincode is the same as that contained in the compound which is undergoing decomposition, the original compound is reproduced. For instance, if a quantity of fused argentic chloride (AgCl) be decomposed by a current which is conducted into it by means of silver wires, the quantity of the chloride will undergo no alteration; for in this experiment, as fast as the silver is deposited upon the negative wire, a corresponding quantity of silver will be dissolved from the positive wire, since the latter wire combines with the equivalent quantity of chlorine which is liberated at this point. Let Ag+ represent the positive silver wire, or zincode, by which the current is conveyed into the melted chloride, and − Ag the negative wire: if the brackets in the upper row of symbols which follow indicate the combination before the passage of the current, the lower ones will show the arrangement after the occurrence of the decomposition:—

$$-\mathrm{Ag} \mid \underbrace{\overbrace{\mathrm{AgCl}}\ \overbrace{\mathrm{AgCl}}\ \overbrace{\mathrm{AgCl}}}\ \mid \mathrm{Ag}+$$

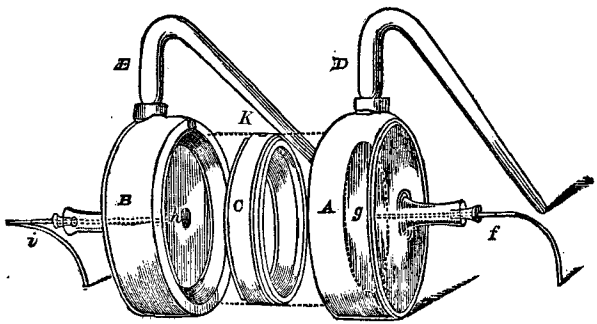
$$\mathrm{AgAg} \mid \underbrace{\overbrace{\mathrm{ClAg}}\ \overbrace{\mathrm{ClAg}}\ \overbrace{\mathrm{ClAg}}}\ \mid$$

An examination of the products furnished by the electrolytic decomposition of aqueous solutions of the oxysalts (or salts formed from acids which contain oxygen), exhibits results which appear to be at variance with the statement that the components of an electrolyte are separated in equivalent proportions—but further investigation shows that they are strictly in accordance with it; these experiments also lead to the very interesting conclusions which have an important bearing upon the theory of salts in general.

When a solution of an oxysalt such as sodic sulphate is sub-

mitted to electrolysis, a quantity of acid accumulates around the positive plate, and of alkali around the negative plate: whilst at the same time both oxygen and hydrogen are set free. The proportions of each may be determined by means of a diaphragm apparatus, in which the products of decomposition can be kept separate from each other, and the gases which are evolved can be separately collected. Such an apparatus was contrived by Daniell, and is represented in fig. 236. A and B are the two halves of a

FIG. 236.



stout glass cylinder, which are fitted by grinding upon a hollow ring of glass, C; the two rims of this ring are ground down to a grooved shoulder, so as to allow a thin piece of bladder to be tied over each end of the ring, which is thereby converted into a kind of drum; at K is a small hole through which the cavity thus formed can be filled with liquid; D and E are two bent glass tubes for carrying off the gases evolved during electrolysis; *g* and *h* are two large platinum electrodes, which pass through corks in the necks of the cylinder, and can be connected with the battery by means of the wires, *f*, *i*. The apparatus thus forms three compartments, which may be filled with the liquid for experiment, and the whole may be supported in a frame of wood. By the employment of this apparatus, it is found that while a quantity of acid accumulates at the zincode, an equivalent quantity of alkali is set free at the platinode. At the same time, a quantity of gas is also emitted from each electrode, that from the zincode being oxygen, and that from the platinode hydrogen. Upon placing a voltameter in the course of the circuit, it is found that a quantity of gas is emitted from the saline liquid, exactly equal to that obtained from the voltameter; and upon neutralizing the acid and alkali, they likewise are in equivalent ratios to the gas which is emitted (Daniell, *Phil. Trans.* 1839, 97, and

1840, 209).* Suppose that the gas collected in the voltameter is 22·32 cubic centimetres (or the quantity yielded by 18 mgrms. of water at 0° C. and 760^{mm}· barometric pressure), the united quantity of oxygen and hydrogen from the solution of sodic sulphate would be the same,—and, in addition, one equivalent in mgrms., or 142 mgrms. of sodic sulphate would be decomposed; 62 mgrms. of soda (Na_2O) would apparently be liberated at the platinode, and 80 mgrms. of sulphuric anhydride (SO_3) at the zincode. Upon substituting a voltameter of fused plumbic chloride in the circuit for one containing diluted sulphuric acid, and still continuing to transmit the current through the solution of sodic sulphate, it was found that for every *equivalent* of plumbic chloride which was decomposed, 1 equivalent of the mixed gases was evolved from the saline solution, and at the same time 1 equivalent of the sulphate was decomposed. What is observed in the case of sodic sulphate holds good, also, with the oxysalts of the alkalies and earths generally.

(286) *Bearing of Electrolysis on the Binary Theory of Salts.*— It is a fundamental law of voltaic action, that the current in any circuit at the same time is equal in every cross section of the circuit, and consequently its decomposing power in each section must also be equal; yet, in the case of sodic sulphate, there appears to be in the saline solution twice as much decomposition that occurs in the adjacent voltameter, although both are transmitting the entire current from the battery. A satisfactory and complete explanation of this anomaly is, however, afforded by the *binary theory* of salts in the following manner :—

Upon the binary theory of salts, the component ions of sodic sulphate are not soda and sulphuric anhydride (Na_2O,SO_3) but sodium and sulphion (a compound of 4 atoms of oxygen and 1 of sulphur), the compound being sodic *sulphionide* (Na_2,SO_4); and such it proves to be under the influence of electrolysis, sodium being liberated at the platinode, whilst sulphion appears at the zincode. Sodium, however, cannot exist in the presence of water; the metal immediately takes oxygen, and becomes converted into soda; $2\,Na_2 + 4\,H_2O$ yielding $4\,NaHO + 2\,H_2$; the alkali is dis-

* This observation is *strictly* true, as I found by numerous careful repetitions of these experiments, although, as Magnus (*Pogg. Annal.* 1857, cii. 1) has pointed out, when the quantity of acid and alkali becomes considerable in the two cells, the liberated acid and alkali each transmit a portion of the current as well as the sodic sulphate, so that if the experiment be unduly prolonged, the portion of the acid and base set free is less than that which theory requires.

solved in the liquid, whilst the hydrogen escapes as gas. Sulphion is equally unable to exist in the separate form; it combines with hydrogen, $2\,H_2O + 2\,SO_4$, becoming $O_2 + 2\,H_2SO_4$, while oxygen escapes, and sulphuric acid is formed; and since both sodium and sulphion are liberated in equivalent proportions, the quantity of water decomposed is also equivalent to the quantity of salt electrolysed.

On the foregoing view, therefore, the evolution of oxygen and hydrogen during the decomposition of such saline solutions is a secondary action. If a solution of a salt of a metal which, like copper or lead, does not decompose water at ordinary temperatures, be substituted for one of sodic sulphate as the electrolyte, no hydrogen should be evolved, but the metal itself should appear upon the platinode; whilst if the other constituent of the salt be one which, like chlorine, is unable to take hydrogen from water at common temperatures, no oxygen should be emitted. Accordingly, upon making the experiment with a solution of cupric or plumbic chloride, the salt is resolved into metallic copper or metallic lead, and chlorine gas, but no oxygen or hydrogen is liberated. These observations will explain the reason that although water, when pure, is scarcely decomposed by the current from 100 cells or upwards, yet it appears instantly to become a good electrolyte on the addition of a few drops of acid, or of solution of a salt of an earth or an alkali; for upon the addition of the salt, it is this body which is decomposed, and the water is then resolved into oxygen and hydrogen by a secondary action in the manner already explained. Sulphuric acid in solution is in like manner resolved into hydrogen and sulphion, H_2 and SO_4. In neither case is the water directly electrolysed. This observation also explains a circumstance which much perplexed the earlier experimenters upon the chemical action of the voltaic pile. In all experiments in which water was decomposed, both acid and alkali were invariably found to be liberated at the electrodes, although distilled water was employed; and hence it was believed for some time that the voltaic current had some mysterious power of generating acid and alkaline matter. The true source of these compounds, however, was traced by Davy (*Phil. Trans.* 1807, 2), who showed that they proceeded from impurities contained either in the water employed, or in the vessels made use of, or in the atmosphere itself. Having proved that ordinary distilled water always contains traces of saline matter, he redistilled it at a temperature below the boiling-point, in order to avoid all risk of carrying over salts by splashing: he found that when he used

marble cups to contain the water for decomposition, the acid was the hydrochloric and the alkali was soda, both derived from sodic chloride present in the marble itself; when agate cups were used to contain the water, he obtained silica; and when he used gold vessels, he procured nitric acid and ammonia, which he traced to atmospheric air; by operating *in vacuo*, the quantity of acid and alkali was reduced to a minimum, but the decomposition then was almost arrested, although he operated with a battery of 50 pairs of plates 4 inches (10 centimetres) square. Hence it is manifest that water itself is not an electrolyte, but it is enabled to convey the current if it contain only faint traces of saline matter.

The following Table illustrates the manner in which saline bodies may be classified in relation to their mode of electric decomposition; the *anion* indicating the electro-negative, the *cathion* the electro-positive component.

A, Simple			Simple Anion	Ag,Cl.
			Simple Cathion	
B, Complex ...	I. Monobasic.	1.	Simple Anion	H_4N,Cl.
			Compound Cathion	
		2.	Compound Anion	K,NO_3.
			Simple Cathion	
		3.	Compound Anion	$H_4N,C_2H_3O_2$.
			Compound Cathion	
	II. Polybasic.	1.	Compound Anion	Na_3,PO_4.
			Simple Cathions	
		2.	Compound Anion	$(Na,H,H_4N)PO_4$.
			Simple and Compound Cathions	

When the solutions of the *monobasic salts* are the subjects of electrolysis, the proportion of acid and base liberated is in single equivalents; for example, a solution of potassic nitrate yields 1 molecule of potash and 1 of nitric acid, for each molecule of fused argentic chloride, which is decomposed in a separate voltameter included in the same circuit. 2 AgCl, and 2 $KNO_3 + 3\,H_2O$ become respectively separated into Ag_2, with Cl_2, and $H_2 + 2\,KHO$ with 2 $HNO_3 + O$.

When an aqueous solution of a dibasic salt, such as sodic sulphate (Na_2SO_4), is submitted to electrolysis, for each molecule of the salt decomposed, 2 molecules of argentic chloride would simultaneously undergo electrolysis, if included in the same circuit; 2 AgCl becoming Ag_2 and Cl_2, while $Na_2SO_4 + 3\,H_2O$ yield

2 $NaHO + H_2$ at the platinode, together with $H_2SO_4 + O$, which appear at the zincode.

Again, 1 molecule of fused plumbic iodide PbI_2, would undergo decomposition, whilst 2 molecules of argentic chloride would, if included in the same circuit, be at the same moment resolved into its elements; 2 AgCl becoming Ag_2 and Cl_2, whilst PbI_2 yield Pb and I_2.

In an analogous manner when a tribasic salt, such as trisodic phosphate (Na_3PO_4), is subjected to electrolysis, the same current which would decompose 2 molecules of the phosphate would simultaneously liberate the chlorine and silver from 6 molecules of argentic chloride in the voltameter; 6 AgCl becoming 3 Ag_2 and 3 Cl_2, and at the same time 2 $Na_3PO_4 + 9\ H_2O$ yield 6 NaHO and 3 H_2 at the platinode, whilst 2 H_3PO_4 and 3 O appear at the zincode.

It will be seen that the proportion of the various elements set free by electrolysis corresponds in each case to the *equivalent*, but not to the *atomic weight*.

This principle may be still further exemplified in other modifications of the phosphates. When a solution of 1 molecule of sodic pyrophosphate ($Na_4P_2O_7$) with 6 molecules of water (6 H_2O) is electrolysed, 4 molecules of argentic chloride are decomposed in the voltameter, whilst 4 NaHO and 2 H_2 make their appearance at the platinode of the diaphragm cell, and $H_4P_2O_7$ with O_2 are set free at the zincode. When a solution of 2 molecules of sodic metaphosphate 2 ($NaPO_3$) is decomposed with 3 molecules of water (3 H_2O), 2 molecules of argentic chloride are electrolysed in the voltameter, whilst 2 NaHO and H_2 appear at the platinode of the diaphragm cell, and 2 HPO_3 with O is liberated at the zincode. In each case the phosphoric acid thus transferred preserves its tribasic, tetrabasic, or monobasic character, according to the nature of the salt which was electrolysed.

The results of the electrolysis of the monobasic and polybasic oxysalts, it will thus be seen, admit of a simple explanation upon the binary theory. The results of the decomposition of the basic salts are not, however, so easily reconciled with this view. According to E. Becquerel, when basic salts are decomposed,—for each molecule of argentic chloride in the voltameter, 1 molecule of a monobasic acid is liberated at the zincode, whilst all the atoms of base which were previously in combination with the acid are liberated at the platinode. My own experiments upon this point confirm this view, although from a numerous series of

trials on the basic nitrites, basic nitrate, and basic acetates of lead, I always obtained a smaller quantity of plumbic oxide and of metallic lead than was required by theory, if this law held good: probably this deficiency was due to the secondary action of the solution upon the liberated oxide. When, for example, the tribasic plumbic acetate ($Pb\ 2\ PbO,\ 2\ C_2H_3O_2$) was decomposed, employing as the electrodes plates of lead instead of plates of platinum, for every 2 of acetion ($C_2H_3O_2$) which appeared at the zincode, somewhat less than 1 atom of metallic lead and 2 molecules of oxide of lead appeared at the platinode: so that the salt appeared to have undergone decomposition into $Pb + 2\ PbO$ and $2\ C_2H_3O_2$. It is difficult to reconcile the idea of an ion consisting of $Pb + 2\ PbO$* with the binary theory. The most probable explanation appears to be this: viz., that the plumbic oxide is attached to the normal acetate in a manner analogous to water of crystallization, and that the normal acetate is the true electrolyte, whilst the oxide is left upon the electrode in the insoluble form as soon as the acid which kept it in solution is removed. A similar explanation may be applied to the case of other soluble basic salts.

Faraday's principle, 'that if the same pair of elements unite with each other to form more than one compound, it is only the compound which contains one atom of each element that admits of electrolysis,' although generally true, if we substitute the expression equivalent for that of atom, cannot, however, be laid down as a law of electric decomposition. It occasionally happens that two different electrolytes containing the same elements exist. Both cupric chloride ($CuCl_2$) and cuprous chloride (Cu_2Cl_2), for example, are electrolytes. When a current of given strength is transmitted successively through, 1, a solution of cupric sulphate; 2, a solution of cupric chloride; and 3, fused cuprous chloride,—decomposition takes place simultaneously in each; but for each molecule of cupric sulphate resolved into Cu and SO_4 one of cupric chloride is decomposed into Cu and Cl_2, and one of cuprous chloride into Cu_2 and Cl_2; so that for each atom of copper separated at the platinode from the solution of the sulphate, and from

---

* E. Becquerel considered that he had obtained a new suboxide of lead by the electrolysis of its basic salts. But this appears to be an error. It is a mere mixture of metallic lead with plumbic oxide, for the solution of the normal plumbic acetate quickly dissolves the oxide and leaves the metallic lead; and the proportion of oxide to the metallic lead varies according to the nature of the salt operated upon.

the cupric (or ordinary) chloride, 2 atoms of copper are liberated from the cuprous chloride.

If cupric sulphate be used as the measure of the voltaic action, Buff (*Liebig's Annal.* 1859, cx. 257) considers when fused molybdic anhydride is electrolysed, that for each molecule of cupric sulphate resolved into Cu and SO_4, 1 molecule of molybdic anhydride (MoO_3) furnishes 1 atom of oxygen and 1 of MoO_2, and in like manner 1 molecule of fused vanadic anhydride (VO_3) furnishes 1 of oxygen and 1 of VO_2.* Fused potassic dichromate ($K_2Cr_2O_7$, or K_2CrO_4,CrO_3) is also an electrolyte, and it is decomposed partially into K_2 and CrO_4, and partially into Cr_2O_3 and O_3.

The same current which liberates 3 atoms of metallic copper from 3 of cupric sulphate, will successively resolve 1 molecule of aluminic chloride (Al_2Cl_6) into Al_2 and Cl_6, 3 of cuprous chloride, 3 Cu_2Cl_2, into Cu_6 and Cl_6, and 2 of chromic anhydride, 2 CrO_3, into Cr_2O_3 and O_3. And it may be stated generally, as indicated by E. Becquerel, that each equivalent of electricity causes the evolution of one equivalent of the electro-negative element, or anion, upon the positive electrode.

When more than one salt is present in solution, the current, when below a certain strength, decomposes only one of them, the best conductor being decomposed when the current is feeble; but when the intensity of the current passes a certain limit, a portion of the inferior conductor also experiences decomposition. This limit to the intensity of the current, according to Magnus (*Pogg. Ann.* 1857, cii. *loc. cit.*), varies with the size of the electrodes, and with the distance between them, as well as with the proportion in which the different electrolytes are mixed.†

(287) *Unequal Transfer of Ions during Electrolysis.*—A curious circumstance in relation to the proportion in which the ions of the electrolyte travel towards the respective electrodes, was remarked in the course of these investigations on the decomposition of saline solutions. It was perhaps natural to expect that, if a solution undergoes electrolytic decomposition, for each equivalent

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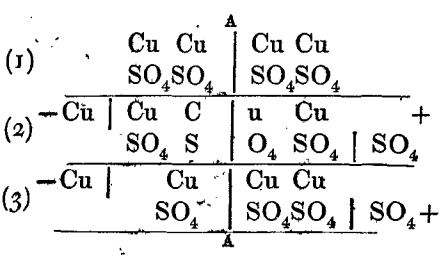
* As vanadic anhydride is now usually represented by the formula V_2O_5(V = 51), it would appear that the body produced by its electrolysis is not a simple oxide of the metal.

† The results obtained by Magnus upon the decomposition of iodic acid, stannic chloride, and some other bodies, appear to be only secondary actions, not produced by the direct electrolysis of these compounds, and consequently they do not admit of being applied to the general theory. This, indeed, has already been pointed out by Buff.

of the compound decomposed, its component ions should be *transferred* to each electrode in the exact proportion of half an equivalent of each, although a whole equivalent was *liberated* in the manner shown at No. 2 in the scheme which follows:—



In this scheme it is supposed that cupric sulphate is the electrolyte, each atom of copper represented by the symbol Cu being in combination with the quantity of sulphion represented by SO_4 immediately beneath it. Let AA indicate the position of a diaphragm of bladder separating two equal quantities of the solution which in No. 1 are supposed to be in their normal state. Let No. 2 represent the same solution after it has undergone electrolysis; an equivalent of copper having been set free at the platinode, and one of sulphion at the zincode. It was not unnatural to expect that this result would have been attained by the transfer of half the quantity of copper into the division containing the platinode, whilst half the equivalent of sulphion passed towards the zincode in the manner represented. Experiment, however, shows that such a supposition is erroneous, and that the decomposition more commonly happens in the mode represented in No. 3, in which case the whole amount of the anion is transferred to the zincode, leaving the corresponding equivalent of cathion uncombined, at the platinode. Sometimes when the oxide of a metal is soluble in water, the transfer of a small quantity of the cathion takes place towards the platinode, but the quantity of the cathion and the anion *set free* are always in equivalent proportions to each other (Daniell and Miller, *Phil. Trans.* 1844, 19). Acids, whether they be soluble in water or not, always travel towards the zincode in proportions larger than those in which the metals united with them pass towards the platinode.

D'Almeida (*Ann. Chim. Phys.* 1857 [3], li. 263) attributes these remarkable irregularities, which occasion much inconvenience in electro-plating, to the development of free acid around the zincode. He considers that the acid, owing to its superior conducting power, conveys a large proportion of the current, and

that the metal is then reduced upon the platinode by the hydrogen, at the moment of its liberation. He finds that when the solutions are strictly neutral the inequality of transfer is scarcely perceived. Strictly neutral solutions of copper and zinc, when decomposed between electrodes of copper or zinc respectively, become acid during the operation, because the metal at the zincode is not dissolved quite so rapidly as it is separated at the platinode, and consequently a little free acid accumulates around the zincode, and occasions the irregularity in transfer of the ions which we are now considering. When a current traverses a saline solution kept constantly acid in the zincode cell, whilst the platinode is maintained constantly neutral, the salt is transferred unequally, the zincode becoming least impoverished; but if the solution be kept neutral around the zincode whilst it is maintained alkaline around the platinode, the result is reversed, and the impoverishment of the platinode is the least marked.

This explanation of D'Almeida is confirmed by the subsequent researches of Magnus. Hittorf (*Pogg. Annal.* 1853, lxxxix. 177, and 1856, xcviii. 1) gives a different, and, as it seems to me, an improbable and complicated theory for the explanation of these results; but his experiments appear to be consistent with those already quoted.

(288) *Electrovection*, or *Electrical Endosmose*.—It was observed many years ago by Porrett (*Annals of Philosophy*, 1816, viii. 74), when water was placed in a diaphragm apparatus, one side of which was connected with the positive, and the other side with the negative electrode of the battery, that a considerable portion of the liquid was transferred from the positive towards the negative side of the arrangement. It has since been found that the same result occurs in a minor degree when saline solutions are electrolysed, and, generally, the greater the resistance which the liquid offers to electrolysis the greater is the amount which is thus mechanically carried over. From numerous experiments I have found that in all these cases the water carries with it a proportion of the salt which it holds in solution. It appears from the researches of Wiedemann (*Pogg. Annal.* 1852, lxxxvii. 321), which have been confirmed by those of Quincke, that the amount of liquid transferred, *cæteris paribus*, is proportioned to the strength of the current; that it is independent of the thickness of the diaphragm by which the two portions of liquid are separated; and that when different solutions are employed, the amount transferred in each case, by currents of equal strength, is directly proportional to the specific resistance of the liquid.

This transfer has been minutely studied by Quincke, who seems to have explained the steps which attend its production:—

If a capillary tube, bent into the form of the letter U, filled with an imperfect conductor, such as alcohol or distilled water, be connected by platinum wires with the inner and outer coatings of a charged Leyden jar, the level of the liquid is raised in the negative limb and depressed in the positive limb. The quantity of liquid which is thus carried over is proportioned to the electromotive force of the arrangement, and is independent of the length of the tube: he has also found that the quantity of liquid carried over for equal charges is inversely as the square of the diameter of the tube. In a syphon tube of one millimetre diameter, connected with the two electrodes of a single cell of Grove's battery, distilled water rises $0{\cdot}^{mm}{\cdot}000061$ in the negative tube.

If oil of turpentin or carbonic disulphide be substituted for water, and the two platinum wires be connected with the positive and negative conductors of the electrical machine, the movements are reversed, the fluid rising in the positive bend. The motion of oil of turpentin may, however, be reversed, if the tube be lined with sulphur. If a diaphragm apparatus with a porous clay septum be used, the essence of turpentin is transferred towards the positive electrode, but if a diaphragm of flowers of sulphur, compressed between two pieces of silk, be used, the transfer is towards the negative electrode. It is obvious that this transfer is connected with the particular electrical condition assumed by the containing vessel or diaphragm, in relation to the liquid which is set in motion.

It has been observed by Jürgensen, that light particles of various solids in suspension in water are transferred in the direction opposite to that in which the water is carried under the influence of the current; and these motions are diminished by the addition of any salt or other substance which increases the conducting power of the liquid.

Into a straight piece of capillary tube $0{\cdot}^{mm}{\cdot}4$ in diameter, let distilled water containing a few granules of starch in suspension be placed, and let the liquid be connected with the positive and negative conductors of the machine, by means of platinum wires sealed into the tube. It will then be seen that the granules in the centre of the tube pass towards the negative electrode, whilst along the sides of the tube a return current occurs towards the other electrode. By increasing the rapidity of the rotation of the machine, the central current becomes increased in rapidity, whilst

that on the surface becomes slower, and at length the movement of the suspended particles is reversed, so that all move towards the negative electrode. The wider the tube, the more difficult it is to produce this reversal of the current of the particles at the surface. Solid particles of the most varied description exhibit these phenomena, and always in the same order when water is employed. For example, whether finely-divided gold, platinum, copper, iron, graphite, quartz, felspar, oxide of manganese, asbestos, emery, baked clay, sulphur, lac, silk, cotton, lycopodium, carmine, quill, paper, ivory, air-bubbles, small drops of oil of turpentin or of carbonic disulphide be used, the phenomena are in each case similar.

If oil of turpentin be substituted for water, the same bodies all move, but the motions are now towards the positive electrode, with the single exception of sulphur.

Quincke seems to have found the key to these remarkable phenomena. By employing granules of lycopodium, which are sufficiently uniform in size, and very nearly of the same density as water, he ascertained by watching their motion under the microscope, that the velocity of a particle near the axis of the tube is proportional to the strength of the current. The following is his explanation:—

The water near the sides of the tube is transferred towards the negative electrode, while all the suspended particles are impelled towards the positive electrode. These two motions are effected with a speed proportioned to the strength of the current; but the water, as there is no other course open to it, returns along the axis of the tube, and assists the motions of the suspended particles. The water on the sides of the tube, on the contrary, carries the particles in a direction opposite to that in which they are tending. When the strength of the electricity increases, the rapidity with which the particles move increases more rapidly than the motion of the liquid, because of the increasing influence of the friction of the sides of the tube upon the moving water; so that at length a point is reached in which the solid particles move faster than the opposing current of water.

In these phenomena the water acts partly as a conductor, partly as an insulator. As a conductor traversed by a current, the cylinder of water acquires on its surface a quantity of free electricity, the density of which varies from one section to another; but inasmuch as the conductivity of water is imperfect, time is required for the communication of the electricity of one particle to the adjacent particles. Now a particle of water near the side

of the tube becomes positively electric by contact with the glass, and its positive electricity tends to move in the same direction as the positive electricity of the current; but since the particle of water cannot instantaneously part with its electricity, it is carried forward in the direction of the positive current: and these motions can only occur in imperfect conductors, which retain their charge for a sensible time. If a foreign substance, such as a grain of starch, be suspended in the water, it becomes negatively electric by simple contact with the water, and independently of the current from the machine,—water having been shown, by Faraday and others, to become positively electrified by friction with every substance hitherto tried; and when two bodies become electric by contact, the electricity which each acquires is the same as that developed by rubbing them together. If a conducting liquid be added to the water, these conditions of the development of electricity by contact are altered, and the motion of the particles is arrested.

Oil of turpentin, on the contrary, becomes negative by friction and by contact with all substances hitherto tried, except sulphur, and consequently the direction of the movements is reversed. (Quincke, *Ann. Chim. Phys.* 1861 [3], lxii. 381, and [3], lxiii. 479.)

(289) *Secondary Results of Electrolysis.*—The explanation already given of the mode in which the oxysalts are electrolysed was happily applied by Daniell to the elucidation of the origin of the voltaic power, in a combination contrived by Becquerel (262), which presents many interesting peculiarities. If a porous tube filled with nitric acid be plunged into a vessel containing a solution of potash, and the wires of a galvanometer, armed with platinum plates, be plunged one into the nitric acid, and the other into the alkaline solution, a current will circulate; oxygen will be emitted from the plate immersed in the potash, and nitrous acid, owing to the absorption of hydrogen by the nitric acid, will be formed around the other plate, whilst potassic nitrate is slowly produced by transudation of the two liquids through the pores of the diaphragm. By connecting several of these cells together in succession, upon the principle of the ordinary battery, the power may be considerably augmented. The decomposition which appears to occur is represented by the following symbols, in which H,NO_3 indicates the nitric acid, and K,HO the potassic hydrate: the position of the brackets above the symbols indicates the arrangement before the current is established, whilst after its

passage, the arrangement is supposed to be that indicated by the brackets beneath :—

$$\overbrace{H,NO_3}\ \overbrace{H,NO_3}\ |\ \overbrace{K,HO}\ \overbrace{K,HO}.$$

It is particularly to be observed that no development of oxygen or of hydrogen occurs upon the platinum plates until the two plates are united by a conducting wire, and it ceases as soon as the conducting communication between the plates is interrupted: in the latter case the polar arrangement of the particles is interfered with, although the reaction of the caustic potash upon the nitric acid continues. The secondary action of the nitric acid on the hydrogen which is set free is necessary to the development of the current. If sulphuric acid be substituted for the nitric, the hydrogen is not absorbed, and no current is obtained, probably because it is neutralized by the counter-current which the accumulation of the hydrogen upon the platinum plate tends to produce (264).

The secondary actions of the voltaic current are often of great importance; they require to be carefully distinguished from its primary effects. Secondary results are, in some instances, produced by the action of the liberated components of the electrolyte upon the materials employed as electrodes: for example, if a slip of copper be substituted for one of platinum, as the zincode of the battery, and be immersed in diluted sulphuric acid, cupric sulphate will be formed by the combination of the copper with the disengaged sulphion. At other times, the secondary results are manifested by the reaction of the ion upon the liquid in which the electrolyte is dissolved, as when the potassium or sodium, set free at the platinode in an aqueous solution of its salts, liberates hydrogen by its action upon the water; $K_2 + 2\ HHO = H_2 + 2\ KHO$. In the cases just cited, the chemical attractions of the disengaged ions are very intense, and the secondary action is exactly proportioned to the primary; so that it may be employed as a measure of the current: but when the tendency to combination is more feeble, the proportion of these secondary actions to the primary one is greatly influenced by the extent of surface exposed by the electrode to the liquid, and by the energy of the current, and consequent quantity of the ion disengaged at once. Generally, the slower the action, and the larger the surface of the electrode, the more uniform and complete is the secondary action. The results are well exemplified

by Bunsen's researches on the isolation of the more oxidizable metals by the voltaic current. If a thin platinum wire be used as the platinode in a solution of chromic chloride, to convey the current from 4 or 5 cells of the nitric-acid battery, metallic chromium may be obtained without difficulty: but if a plate of platinum be employed, chromic oxide, mixed with a certain amount of hydrogen, is liberated; in the latter case the metal has time to decompose the water before fresh particles of chromium are deposited upon its surface.

In consequence of these secondary actions, the same element may sometimes appear at one electrode, sometimes at the other, as is seen in the case of nitrogen: if, for instance, a solution of ammonic sulphate be submitted to electrolysis, it yields ammonia and hydrogen at the platinode, and a mixture of nitrogen with oxygen is set free at the zincode. The nitrogen in this case is liberated as a secondary result of the combination of a portion of the oxygen with the hydrogen of the ammonia. If ammonic nitrate be substituted for the sulphate, nitrogen appears among the gaseous products at both electrodes, the nitric acid being deprived of its oxygen by the hydrogen evolved at the platinode, and the ammonia of its hydrogen by the oxygen set free at the zincode.

If a solution of plumbic acetate be employed as the electrolyte, the acetic acid undergoes partial decomposition from the action of the oxygen upon it at the moment of its liberation at the zincode, but at the same time a portion of the oxygen also enters into combination with some of the plumbic oxide contained in the liquid, and, as Warrington proved, a deposit of plumbic dioxide (PbO_2) is produced. Nobili, who first observed this phenomenon, found that if a polished steel plate be employed in such a solution as the zincode to the battery (4 or 6 cells of Grove's may be employed), the deposit assumes the form of a thin film, which exhibits the iridescent tints of Newton's scale,—the tints varying according to the thickness of the film produced. Other experimentalists have modified the patterns which may be obtained by these *metallochromes*, which have been applied by Becquerel even to the imitation of the tints of flowers; and by varying the strength of the battery and of the solutions employed, he has succeeded in producing some effects of great delicacy and beauty. Salts of manganese or of bismuth may be substituted for those of lead, with similar results.

Many of these secondary actions are very interesting: Kolbe has devoted particular attention to the effects of oxygen when

liberated during electrolysis (*Mem. Chem. Soc.* 1846, iii. 285, and *Q. J. Chem. Soc.* 1849, ii. 157). Hydrochloric acid, especially when previously mixed with sulphuric acid, is in this manner partially converted around the zincode into chloric and perchloric acids; and in an acid solution of potassic chloride, potassic chlorate and perchlorate are formed. Potassic cyanide in solution, when subjected to the voltaic current, is in like manner converted into the cyanate. A concentrated solution of sal-ammoniac (H_4NCl) evolves hydrogen at the platinode, but the chlorine, instead of being liberated at the zincode, acts upon the sal-ammoniac, and forms oily drops of the so-called chloride of nitrogen, which explode when touched by the opposite electrode. Smee has shown that by means of the voltaic current the ferrocyanide may be converted into the ferricyanide of potassium. Kolbe has, further, ascertained the effect of the liberated oxygen upon various organic compounds, and by submitting potassic valerate ($KC_5H_9O_2$) to electrolysis he decomposed the radicle of valeric acid ($C_5H_9O_2$) which it contains, and succeeded in obtaining from it a new substance *valyl* $(C_4H_9)_2$, (or more properly *tetryl*); a new ether, ($C_8H_{18}O$) *tetrylic ether*, and a hydrocarbon (C_4H_8), apparently identical with oil-gas: and by a similar process from acetic acid ($HC_2H_3O_2$) he obtained methyl $(CH_3)_2$, the homologue of tetryl. Particular interest is attached to these researches, owing to the circumstance that in each case the compounds obtained by the electrolysis belong to a series related to an alcohol different from that which was submitted to decomposition. The valerates thus yield an ether of the tetrylic series, and the acetates, which are derivatives of wine-alcohol, furnish a hydrocarbon which belongs to the wood-spirit series.

(290) *Nascent State of Bodies.*—It is obvious, from the powerful effect which oxygen produces at the moment of its liberation from compounds during electrolytic decomposition, that such oxygen must be in a condition very different from that in which it exists when once it has assumed the gaseous form. Oxygen is not insoluble in water, and it is therefore possible to bring it in small quantities at a time into chemical contact with salts or other bodies which water may hold in solution. Oxygen gas may, however, be passed for an unlimited time through a solution of potassic chloride without effecting the conversion of any portion of the chloride into chlorate, or into perchlorate of potassium; and yet, as has been mentioned in the foregoing paragraph, this change is easily effected by oxygen as it escapes during the electrolysis of an acidulated solution of potassic chloride.

But it is not necessary that oxygen should be liberated by the agency of the voltaic battery in order that it should acquire this increase of activity. If hydrated nickelous or cobaltous oxide be suspended in a solution of caustic potash, it will undergo no change when subjected to a current of oxygen gas; but if a current of chlorine be substituted for the oxygen, the whole of the metallic oxide will be converted into a brown sesquioxide; this change arises from the action of the chlorine upon the potash, during which, potassic chloride is formed, whilst oxygen is set free, and at the moment of its liberation attaches itself to the nickelous or cobaltous oxide, $2KHO + Cl_2 + 2(NiO,H_2O) = 2KCl + Ni_2O_3,3H_2O$. Other substances besides oxygen exhibit this peculiarity, and chemists have long recognized the fact that bodies, when in this *nascent state*—that is to say, when in the act of liberation from other substances—display more energetic attractions than they show when once obtained in the isolated form:—For example, cyanogen and chlorine do not enter directly into combination; but if cyanogen at the instant that it is set free from another compound, be presented to chlorine, the two bodies combine; so that if moist mercuric cyanide be decomposed by means of chlorine, chloride of cyanogen may be obtained: the chlorine removes the mercury step by step, and the cyanogen at the moment of its liberation enters into combination with another portion of chlorine. In a similar manner, sulphur when set free from an alkaline persulphide in the midst of a solution of hydrochloric acid, combines with hydrogen, and forms persulphide of hydrogen, $K_2S_2 + 2\,HCl = H_2S_2 + 2\,KCl$, the chlorine taking the potassium, whilst the sulphur and the hydrogen, both in the nascent state, unite to form a new compound, although their chemical attraction is so slight that this compound separates spontaneously into sulphuretted hydrogen and free sulphur. The process of double decomposition is particularly applicable in cases where the mutual attraction of the bodies which it is desired to obtain in combination is comparatively feeble. It is not impossible that this superior chemical activity of bodies in the nascent state may arise from the fact that their particles are individually electrified at the moment of their separation from a previous state of combination; and that in this condition they may exert upon the particles of dissimilar contiguous matter, a force of induction which may be the agent that determines their chemical combination: if by a process of *double* decomposition the particles of both compounds were oppositely electrified, combination might be expected to be proportionately facilitated:—For instance, if a solu-

tion of potassic sulphide and one of cupric chloride be mixed, they will decompose each other; the sulphur being negative, will tend to combine with the positive copper, and the positive potassium to unite with the negative chlorine. If the brackets in No. 1 represent the mode in which the molecules are arranged on the instant of mixture previous to decomposition, those in No. 2 will illustrate the arrangement of the molecules after mutual decomposition has been effected:—

$$(1)\quad \begin{matrix} \overbrace{\overset{+}{K_2}\overset{-}{S}} & \overbrace{\overset{+}{Cu}\ \overset{-}{Cl_2}} \\ \underbrace{\overset{-}{Cl_2}\overset{+}{Cu}} & \underbrace{\overset{-}{S}\ \overset{+}{K_2}} \end{matrix} \text{ become } \left\{\begin{matrix} \overset{+}{K_2} & \overbrace{\overset{-}{S}\ \overset{+}{Cu}} & \overset{-}{Cl_2} \\ \underset{-}{Cl_2} & \underbrace{\overset{+}{Cu}\ \overset{-}{S}} & \underset{+}{K_2} \end{matrix}\right\}(2)$$

(291) *Theory of the Electrical Origin of Chemical Attraction.*—It has already been remarked (245, 257) that whenever two dissimilar substances, electrically insulated, are first brought into contact, and are then separated from each other, disturbance of their electrical equilibrium is produced; one of the bodies becoming negatively electrified whilst the other acquires a corresponding charge of positive electricity. It is a well ascertained fact, that certain substances, by friction, acquire one kind of electricity more readily than the other; sulphur, for example, when rubbed upon flannel or fur, becomes negatively electric, whilst glass, on the other hand, most readily assumes the positive state. What has been proved to occur when masses of matter are brought into contact was supposed by Davy (*Phil. Trans.* 1807, 39) to happen also when the molecules of two dissimilar substances are brought within the sphere of mutual activity: he assumed 'that chemical and electrical attractions depend upon the same cause, acting in one case on particles, in the other on masses of matter' (*Phil. Trans.* 1826, 389); and all the phenomena of chemical attraction have been referred to the exertion of mutual electrical attraction between the atoms of each substance in the compound. When, for example, chlorine and potassium are united, it is supposed that each atom of chlorine, by contact with an atom of potassium, becomes negatively electrified, whilst the potassium becomes positively excited; a certain portion of the positive electricity from the chlorine uniting with a corresponding amount of negative electricity which is liberated from the potassium, thus producing the light and heat which attends the combination of these two bodies (Berzelius). Supposing each atom of both kinds of matter to be associated with equal quantities of both electricities, and that the two different electricities be represented by

the signs + and −, we may represent the potassium and chlorine by symbols; (− K +) indicating an atom of potassium, and (− Cl +) an atom of chlorine. As soon as the two bodies are brought into contact, it is supposed that the chlorine loses a certain amount of positive electricity, whilst the potassium loses an equal quantity of negative electricity, the change being symbolized thus (+ KCl −) and (+ −). When the potassic chloride is decomposed electrolytically, a quantity of positive electricity is transferred from the positive wire of the battery to the chlorine, and compensates for that which it lost in the act of combining; and when this amount of electricity has been restored, the chlorine no longer has any tendency to remain in combination with the potassium, and hence it is set free upon the positive plate, whilst a simultaneous transfer of negative electricity to the potassium occurs from the negative plate, and the alkaline metal is therefore liberated upon the negative side of the arrangement. The electricity which is set free by the battery is supplied by the action of the sulphion upon the zinc, in the cells of which the battery consists.

The remarkable law discovered by Faraday, that the same current of electricity when transmitted successively through various electrolytes, decomposes each in the proportion of their respective chemical equivalents (282, iv.) adds greatly to the probability of the supposition that electrical and chemical phenomena are due to different manifestations of the same cause. So strong was Daniell's conviction upon this point, that he applied the term *current affinity* to the voltaic current; since by means of the proper application of conductors, or channels for the force, the chemical attraction of a portion of zinc and sulphuric acid at one point could be transferred to a distant spot, and could there be made to effect an equivalent amount of chemical decomposition upon a different compound. Upon the electro-chemical theory, the chemical equivalent of any substance is that quantity of each body which is associated with an amount of electricity equal to that associated with a given weight of some substance, such as hydrogen, which is selected as the standard of comparison; the proportion of electricity which is associated with a given weight of any substance being inversely as its chemical equivalent, not its atomic weight. Assuming the specific electricity of hydrogen to be represented by the arbitrary number 1000, the following is given by Daniell (*Introd. to Chem. Phil.* 1843, 2nd Ed. 687) as an approximate table of the *specific electricity* (or quantity of elec-

tricity associated with *equal weights*) of a few of the more important elements and compounds:—

Cathions.	Equivalent.	Specific Electricity.	Anions.	Equivalent.	Specific Electricity.
Hydrogen ...	1·0	1000	Oxygen ...	8·0	125
Potassium ...	39·2	25	Chlorine ...	35·5	27
Sodium ...	23·3	43	Iodine	126·0	8
Zinc	32·5	31	Bromine ...	78·3	12
Copper... ...	31·6	31	Fluorine ...	18·7	55
Ammonia ...	17·0	58	Cyanogen ...	26·0	38
Potash... ...	47·2	21	Sulphuric Acid	40·0	25
Soda	31·3	32	Nitric Acid ...	54·0	18
Lime	28·5	35	Chloric Acid	75·5	13

Ingenious, however, as is the electrical theory of chemical attraction, it must be admitted that it is far from being free from objection and difficulty when an attempt is made to apply it to all cases of chemical action. It has been already stated that a very large number of bodies exist which are not susceptible of electrolysis.* Indeed, the chief classes of electrolytes are: 1, binary, compounds of the non-metallic elements with the metals, such as the oxides, chlorides, iodides, bromides, and fluorides; 2, compounds of the metals with bodies like cyanogen, such as the cyanides and the sulphocyanides; and 3, compounds of the metals with the *oxions* or radicles of the oxyacids, such as the nitrates, sulphates, borates, carbonates, acetates, tartrates, &c. Now, as long as a compound consists of two elements only, if it be decomposed at all, there is no difficulty in anticipating the result of the voltaic action:—the electro-negative element will appear at the zincode, and the electro-positive element at the platinode; yet there are compounds consisting of two elements only which are not electrolysable, such, for instance, as pure water, and sulphur chloride (S_2Cl_2). If their particles be united by electric opposition, why

* In the experiments of Lapschin and Tichanowitsch (*Phil. Mag.* 1861 [4], xxii. 308) a very numerous series of Grove's battery, amounting to 900, and in some instances even to 950 pairs, produced no effect on absolute alcohol, ether, valeric acid, oil of turpentin, carbonic disulphide, or fused boracic anhydride: fusel-oil was scarcely acted on. Bleekrode (*Proc. Roy. Soc.* 1876, xxv. 322) has experimented with Mr. De La Rue's battery of 8040 cells on liquefied ammonia, carbonic disulphide, benzol, stannic chloride, liquefied carbonic anhydride, liquefied hydrochloric acid, cyanogen, and zinc-ethyl. The ammonia was decomposed with the formation of a deep blue colour, which rapidly disappeared when the current was stopped, and zinc-ethyl also showed signs of electrolysis. The other liquids were unaffected.

should they not yield to the current? In the case of more complex bodies, such, for example, as argentic nitrate or plumbic borate, it is not possible, *à priori*, to say how the compound would yield under the electric influence. It is quite clear in the case of a salt, that the power which holds together the two ions of the salt in the form of two *iso-electric* groups (or groups of equal electric energy), must be of a different order from that which holds the elements of its component ions in combination. The tie which binds together argentic nitrate as $AgNO_3$, must be of an order different from that which unites the elements of *nitrion* (NO_3) together. Sodic sulphate, again, as an electrolyte is separable into Na_2 and SO_4. But neither nitrion nor sulphion can exist in the separate form; how can they become associated under electric influence? Again, sulphuric anhydride (SO_3) is not an electrolyte when fused: the same thing may be said of fused boracic anhydride; and examples of this kind might be multiplied almost without limit. Why, if chemical attraction be due to the exertion of electric action, should certain bodies be readily decomposable by the voltaic current, and why should others of less complex composition resist it entirely? At present, no hint appears to have been given which offers any clue to the solution of these questions.

Practical Applications of Electrolytic Action.

(292) *Electrotype, Voltatype,* or *Galvano-Plastics.*—Shortly after Daniell had invented his constant battery, he observed that when copper was deposited upon a plate of platinum, it furnished a coherent sheet in which the lines and irregularities on the surface of the platinum were faithfully reproduced upon the deposited copper; but he made no practical application of the observation. In the year 1839, Jacobi, of St. Petersburg, announced that he had discovered a method of making exact copies of a metallic surface in copper by means of the voltaic battery, and shortly afterwards Messrs. Spencer and Jordan, who had each independently arrived at a similar result, published the methods which they had employed for the attainment of this object. The processes thus disclosed were so simple and easy of execution that they were immediately repeated with success; and in the following year Mr. Elkington in England, and M. Ruolz in France, began to apply the voltaic battery on an extensive scale to the arts of plating and gilding. Since this period the voltaic battery has been most extensively employed as a means of depositing not only copper, gold, and silver from their solutions, but zinc, tin, and lead,

and occasionally platinum and nickel: many other metals have also, for particular purposes, been reduced from their salts by its means.

For the deposition of metallic copper, a solution of the sulphate of this metal is employed, but the mode of using it varies with the object in view. Suppose that it be desired to obtain a copy of an engraved copper plate; a wire or slip of copper having been soldered to the plate for the purpose of facilitating its connexion with the battery, the back of the plate is covered with a resinous varnish, by which means this surface is electrically insulated from the solution, and it is thus protected from any deposit of reduced metal. The plate thus prepared is connected with the negative electrode of a voltaic battery, consisting of three or four of Smee's or Daniell's cells, and immersed vertically in a bath consisting of a solution of cupric sulphate (sulphate of copper) slightly acidulated and not quite saturated. A sheet of copper, equal in size to the one to be copied, is suspended parallel to the latter in the liquid, and connected with the positive electrode of the battery; an immediate decomposition of the solution ensues; metallic copper is deposited upon the entire surface of the negative plate, in the form of a coherent, continuous sheet, and an amount of copper corresponding closely to this is dissolved from the positive plate, so that the liquid remains constantly charged with a quantity of cupric sulphate approximately equal to that originally employed. At the commencement of the operation, care must be taken to ascertain that the deposit occurs uniformly over the whole surface of the negative plate, for if any portion of it be soiled by grease or resinous matter, the copper will not be thrown down upon those parts; when once the deposition has commenced uniformly, it goes on without difficulty. If the plates be suspended vertically, the solution should be frequently agitated, for unless this precaution be taken, the liquid around the negative plate becomes impoverished, whilst that around the positive plate becomes unduly saturated with the copper salt (287); currents are then produced in the liquid, owing to its unequal density, and they occasion the formation of vertical grooves and striæ upon the back of the sheet of deposited metal. This inconvenience is sometimes obviated by supporting the two plates in the bath in a horizontal position, the negative plate being undermost; the positive plate must in this case be enveloped in flannel, in order to prevent the small particles of metal, which are constantly being detached from it, from falling upon the lower plate, and interfering with the regularity of the deposition.

The deposit varies in hardness and coherence according to the number of cells employed in the battery, the relative size of the plates of the battery and those of the depositing cell, and the temperature and degree of concentration of the solution. The more slowly the action takes place, if the solution be concentrated, the harder and more crystalline is the deposit. By modifying the power of the battery and the strength of the solution, in the manner which experience soon indicates, copper may be obtained of any desired degree of toughness.

When the deposit has attained the necessary thickness, it must be detached at its edges from the original plate, and can then be stripped off without difficulty. The thin film of oxide, or of other adhering impurity, derived from the exposure even of a freshly deposited copper plate to the air for a few hours, is sufficient to prevent too intimate an adhesion between the plate and the deposit. In the electrotype thus obtained, the lines which are cut away upon the surface of the original plate are represented in relief in the copy, and if a fac-simile of the engraving be desired, a new deposit must be formed upon the copy thus procured; in this second transfer, an exact duplicate of the original engraving will be presented. So faithfully does the deposit reproduce all irregularities upon the surface of the matrix on which it is deposited, that by its means copies of daguerreotype plates have been obtained in which the original design is accurately transferred to the deposit of copper, without destroying the original impression. Many large and valuable copper plates, amongst which are some of those engraved for the Art Union, have been electrotyped with success. Bas-reliefs of large size have also been executed, as, for instance, those around the base of the pedestal of Gutenberg's statue at Strasburg; but in such cases the positive electrode must be provided with prolongations, which project into the hollows of the mould, so as to conduct the electricity into the portions of liquid which they contain: without this precaution, the deposit would either not be produced at all in the prominent parts, or it would be too thin.

(293) *Preparation of Moulds for Electrotyping.*—In copying medals or other works of art, it is frequently necessary to employ casts of the objects, instead of the original objects themselves, which might be liable to injury by immersion in the metallic solution. These casts may be made in fusible metal, or in stearin, in plaster, or gutta percha. A mixture of 2 parts of wax, 2 of stearic acid, and 1 of plumbago, is said to give very

good results. Gore (*Pharm. Journal*, 1855, xv. 21) recommends a mixture of 2 parts of gutta percha and 1 part of marine glue; the materials are to be cut up, and the glue melted at a gentle heat and incorporated with the gutta percha. The paste should be applied whilst soft, with a gradually increasing pressure, to the surface of the medal or other object which it is desired to copy. In certain cases an impression of the object to be copied is obtained in sheet lead by the application of strong pressure. In every instance, before proceeding to effect the metallic deposition, the back of the mould, if made of metal, or of a conductor of electricity, must be coated with a resinous varnish, or with some non-conducting matter. When moulds of plaster of Paris are employed, they must be rendered impervious to moisture by immersion in melted wax or tallow; after which the surface to be copied is endued with the power of conducting electricity, by applying finely-powdered plumbago, of good quality, to the surface by means of a brush; taking care that every portion of the surface to be copied is completely coated by it. The cast is then connected with the negative wire of the battery by means of a strip of sheet lead, or a copper wire, which is in electric contact with some portion of the black-lead surface. Impressions of seals in sealing-wax, stamps in relief upon pasteboard or paper, and the engraved blocks used for wood-cuts, after they have been thus rendered conductors upon the surface, may be electrotyped with facility. Even glass may be rendered a conductor by the use of one of the methods of depositing silver upon its surface. Leaves, flowers, fruits, and insects have also been coated with copper, or with silver, by the electrotype process. A mode of producing a conducting surface upon these articles, due to Capt. Ibbetson, consists in immersing them in a weak solution of phosphorus, either in carbonic disulphide or in ether, allowing the solvent to evaporate from the surface, and then plunging the objects into a solution of argentic nitrate; the phosphorus left upon the surface reduces a very thin film of silver upon the superficial portions of the objects, sufficient to enable them to receive the deposit from the battery, if they be properly connected with the negative wire, and submitted in a metallic bath to the action of the electric current. Steel plates cannot be copied by immersing them in a bath of cupric sulphate, because the steel and the sulphate act chemically on each other, and thus the engraving would be destroyed. This difficulty has been overcome by electrotyping them first in silver, which can be deposited upon the steel without injury, and upon

this silver matrix a copper fac-simile of the original plate can afterwards be obtained. More recently Weil has shown that an alkaline solution of cupric tartrate may be employed for depositing at once on cast iron or steel. No battery is needed, but the articles are simply suspended by zinc wires in the bath.

For the electrotyping of small objects, such as coins or medals, it is not necessary to use a separate voltaic battery, since the depositing cell itself may, in the following manner, be converted into a voltaic couple of sufficient power to decompose cupric sulphate:—Let a glass cylinder, such as the chimney of an argand gas-burner, be closed below by a plug of plaster of Paris, and be supported in a vessel containing a solution of cupric sulphate, in which the mould or the medal to be copied is supported by a metallic wire; let the inner tube be filled with sulphuric acid diluted with 10 or 12 times its volume of water, and let an amalgamated zinc rod be placed at its axis. If this zinc rod be connected with the wire proceeding from the mould of the medal to be electrotyped, copper will be deposited upon the surface of the mould. The apparatus in fact constitutes a cell of Daniell's battery, with a trifling modification in its form. The solution of copper should be maintained uniformly saturated with cupric sulphate, by suspending crystals of the salt in the upper part of the liquid.

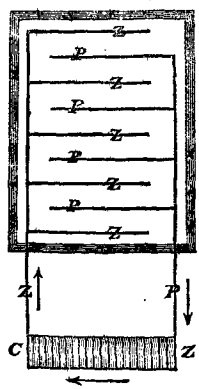
(294) *Electro-Zincing.*—Zinc may be deposited from its sulphate on the surface of iron by processes similar to those used for cupric sulphate. The operation requires but a feeble current, and admits of being performed upon a very large scale: the iron links of the suspension bridge formerly erected at Hungerford, but now transferred to Clifton, which were passed into the abutments on the side of the Thames, were successfully submitted to this operation; each of these links is 24 feet, or nearly 7·5 metres, in length, and of proportionate width.

It is not possible, however, to obtain coherent plates of all the metals with the same facility as is the case with copper and zinc. Many of the metals are thrown down from their solutions in a crystalline form, whether the deposition be effected rapidly or slowly. Silver is separated thus from its nitrate, and lead exhibits a similar deportment when the acetate or the nitrate of this metal is electrolysed. Gold and platinum do not give coherent plates when solutions of the chlorides of these metals are submitted to voltaic decomposition. Lead may be deposited upon iron from a solution of plumbic oxide in potash; and a solution of stannic oxide in potash may be used to obtain coherent

plates of tin by electrolysis. In like manner ammoniacal solutions of the salts of cobalt and nickel may be employed to furnish electrotype plates of these metals. In some cases, however, where a simple salt fails to give a satisfactory result, the effect may be obtained by the employment of certain double salts of the same metal with potassium or with sodium; for this reason auropotassic cyanide ($KAuCy_2$) is largely employed for gilding, and the corresponding salt of silver is extensively used in electro-silvering: iron may be deposited from a solution of the double magnesic ferrous sulphate. (Jacobi, *Report Brit. Assoc.* 1869, 67.) In gilding, silvering, and zincing, one great desideratum is to obtain a firm adherence between the newly-deposited metal and the object to be gilt or plated; the surface of the metallic object is therefore first rendered *chemically* clean, a result which is carefully avoided in the process of electrotyping. In the latter case it is usual to expose the object, if freshly polished, to the atmosphere for 24 hours before placing it in the depositing cell, in order to prevent permanent adhesion.

(295) *Electro-Plating.*—The metals upon which an adherent coating of silver is most readily deposited are brass, copper, bronze, and German silver; but it may also be effected on steel. The articles to be plated are cleansed from adhering greasy matters either by boiling them in a weak alkaline solution, and then washing; or they are heated to low redness in a muffle: in either case they are next dipped into dilute nitric acid for the purpose of removing any adhering film of oxide. They are then brushed with a hard brush and some sand; and having been rinsed from adhering impurities, and separately attached to a clean copper wire, they are again dipped for an instant into nitric acid, washed, and immersed while still wet in the silvering bath. Let fig. 237 represent a plan of this bath, and c z the voltaic battery; the copper wires attached to the articles to be plated are twisted round the rods P P P, which are connected with the negative wire of the battery, whilst the positive wire is connected with a series of silver plates, z z z, which are also immersed in the silvering liquid. This solution is commonly prepared by dissolving argentic cyanide in a solution either of cyanide or of ferrocyanide of potassium. Solutions containing argentic thiosulphate (hyposulphite) or sulphite are occasionally employed.

FIG. 237.



In order to prepare the silvering bath, a solution of argentic nitrate may be precipitated by the addition of potassic cyanide as long as it produces a precipitate: this precipitate, after having been washed by decantation, is dissolved in a solution of potassic cyanide. An excess of potassic cyanide is requisite; at least 3 parts of potassic cyanide being employed for 1 part of argentic cyanide.* A solution which contains $\frac{1}{50}$ of its weight in silver is found to be of a convenient strength for ordinary operations. When potassic cyanide is used in the bath as a solvent, the solution gradually becomes alkaline from the formation of potassic carbonate, which accumulates in the liquid and interferes with the regularity of the decomposition: but if calcic cyanide be substituted for the potassic cyanide, this inconvenience is obviated, since calcic carbonate is formed, and owing to its insolubility, it sinks to the bottom of the bath as fast as it is produced. The articles when plated have a dead white or chalky surface, but they may be burnished by pressure if desired, and they then assume the brilliant lustre of polished silver. It is remarkable that the addition of a very small proportion of carbonic disulphide to the bath causes the deposited silver to assume the lustre of the polished metal.† The amount of silver which is deposited can be regulated very accurately by weighing the articles before immersion, and weighing them again afterwards. A deposit of from 1¼ ounce to 1½ ounce of silver to a square foot of the plated surface (from 4·2 to 5·0 grms. per square decimetre) answers well in practice; the sheet of silver under these circumstances being of about the thickness of ordinary writing paper. The solution must be frequently stirred, in order to preserve the liquid of uniform density and composition throughout.

The batteries used at Birmingham for gilding and silvering are in general simply plates of amalgamated zinc opposed to plates of copper in dilute sulphuric acid: the plates are so arranged that they can be readily raised or lowered in order to expose a smaller

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* If potassic ferrocyanide be used as a solvent of the argentic cyanide, 10 parts of this salt are required for the solution of 1 part of cyanide of silver.

† In order to effect this object, 6 ounces of carbonic disulphide are directed to be agitated with 1 gallon of the plating liquid, and set aside for 24 hours. Two ounces of the liquid thus obtained, are to be added over night to 20 gallons of the ordinary plating liquid; the bath is ready for use next morning. This addition of the solution of the disulphide requires to be renewed daily, to make up for the loss of the carbonic disulphide by evaporation. Much care is required in the use of such a solution, for it is liable to changes which are produced by very slight modifications in the mode of working.

or larger surface to the action of the acid. The superficial area, and number of the plates used, are made to vary according to the size and nature of the objects to be operated upon. The workman judges from experience as to the number of pairs to be employed; it seldom happens that more than two or three pairs of plates are needed. In Paris, Bunsen's carbon and zinc batteries are also employed with success in these operations. Magneto-electric machines (315) are now frequently used instead of batteries.

(296) *Electro-Gilding and Platinizing.*—It is possible to gild most of the ordinary metals by voltaic action. Articles which consist of brass, bronze, copper, or German silver are first annealed, then *pickled,* as the operation of immersing them into the mixture of diluted nitric and sulphuric acids is termed, after which they are scrubbed and 'dipped' in strong nitric acid, and then rinsed in water, as is practised in preparing them for plating. Silver articles are cleansed in a similar manner, but they do not require to be 'dipped.' Iron and steel may be gilt by cleansing them from grease, first with potash, and then by dipping in nitric acid, and scouring the surface with burnt clay finely sifted, in order to remove the black stains produced by the liberation of carbon. A more powerful current is required for gilding upon iron than upon the metals previously mentioned.

The gilding bath most usually employed consists of aurous cyanide dissolved in potassic cyanide. It may be prepared by dissolving gold in aqua regia, and adding potassic cyanide to the diluted liquid so long as it produces a precipitate; a brisk effervescence accompanies the action, and a yellow deposit of aurous cyanide (AuCy) is formed: the clear liquid is decanted, and the precipitate is redissolved in a solution containing between 7 and 8 parts of potassic cyanide to 1 part of gold: the solution is then diluted until 100 parts of the liquid contain 1 part of gold.

M. Ruolz has shown that various other gilding baths may be used instead of the auro-potassic cyanide: for example, he finds that aurous cyanide may be employed when brought into solution by the ferrocyanide or by the ferricyanide of potassium; he has also used with success the aurous sodic sulphite, the solution of the sodic-auric chloride ($NaCl$, $AuCl_3$) or iodide with an excess of soda, and even the sulphide of gold dissolved in a solution of protosulphide of potassium.

As yet the deposition of platinum by voltaic action has not been practised to any considerable extent, but it is said that a solution of the potassic-platinic chloride ($2\ KCl$, $PtCl_4$) in caustic potash may be applied to this purpose with tolerable success.

(297) *Resemblances between the Electricity of the Machine and that of the Voltaic Battery.*—Notwithstanding the extremely brief duration of the discharge from the electrical machine, it produces, whilst it lasts, phenomena similar to those of the voltaic current, which, indeed, may be regarded as a succession of discharges renewed so frequently as to become continuous. By repeating the discharge from the electrical machine many times through the same liquid conductor, Faraday was enabled to obtain true electrolytic decomposition. The following simple experiment may be adduced as an illustration of this fact:—Upon a plate of glass place a small piece of turmeric paper, moistened with a solution of potassic iodide which has been mixed with a little starch; upon one end of this piece of paper allow the point of a fine platinum wire to rest, the other end of the wire being in communication with the prime conductor of the machine; on the other extremity of the paper place a similar wire in communication with the earth: it will be found on setting the machine in action that, after the lapse of one or two minutes, a small blue spot will appear round the point of the wire connected with the prime conductor, owing to the liberation of iodine; while round the wire which communicates with the earth a brown spot will be formed, from the action of the alkali which is set free. If the wires, instead of being connected through the medium of a solution of potassic iodide, be made to dip into a drop of a solution of cupric sulphate, metallic copper will be deposited on the wire connected with the earth, and oxygen and sulphuric acid will appear on the other wire. If a piece of litmus or turmeric paper, moistened with a solution of sodic sulphate, be supported on a thread of glass between two wires, one of which proceeds from the prime conductor, whilst the other is in communication with the earth, the saline solution in the paper will be decomposed by the electricity, even if the paper does not touch either of the wires: the litmus paper on the side towards the prime conductor will gradually be reddened, whilst the turmeric paper will be turned brown at the extremity which is furthest from the prime conductor.

The quantity of electricity which is required to produce chemical decomposition is very great. This fact is strikingly illustrated by a comparison which was made by Faraday between the amount of electricity developed from the machine by friction and that which is furnished by the chemical action of the battery. The experiment was performed in the following manner:—A wire of platinum and another wire of zinc, each $\frac{1}{18}$ of an inch in

diameter, were immersed $\frac{5}{16}$ of an inch apart, to a depth of $\frac{5}{8}$ of an inch in an extremely dilute acid liquid, prepared by adding a single drop of oil of vitriol to four ounces of water. The current obtained from this combination, at a temperature of 15° C., was passed through the coil of a galvanometer consisting of 18 feet of copper wire $\frac{1}{18}$ of an inch thick. It produced in about three seconds as great a deviation of the needle as was obtained by the electricity furnished by thirty turns of a powerful plate-machine in excellent action. This quantity, if concentrated within a space of time constituting only a minute fraction of a second, by discharging it in a single flash from a Leyden battery, exposing 3500 square inches of coated surface, would have been sufficient to kill a small animal, such as a cat or a rat; but the chemical action upon the zinc by which it was produced was so trifling as to be quite inappreciable; and it is estimated by Faraday that not less than 800,000 discharges, each equal in quantity to this, would be required for the decomposition of a single grain of water! Extraordinary as this estimate appears, it has been amply confirmed by later experiments of Becquerel upon this subject: and from the experiments of Weber, it may be calculated that, if the whole of the positive electricity required to decompose a grain of water were accumulated upon a cloud 1000 metres (3281 feet) above the surface of the earth, the attractive force exerted between the cloud and the portion of the earth beneath it would be equal to 1497 tons!

A recent experiment made by Messrs. Warren De La Rue and Hugo W. Müller, of which they kindly permit a description to appear here in anticipation of a paper to be communicated to the Royal Society, illustrates very strikingly the powerful heating effects obtainable from a quantity of electricity sufficient to decompose only a very small quantity of water. A condenser of 44·8 microfarad capacity was charged by 3000 cells of their battery, the current flowing through a voltameter in which only $\frac{1}{5000}$ of a grain of water was decomposed by the electricity which accumulated in the condenser; this charge was, however, capable of deflagrating a piece of platinum wire 8 inches long and $\frac{1}{80}$ of an inch in thickness.

(298) *Deluc's Dry Pile.*—The relation between the electricity of the voltaic battery and that of the ordinary electrical machine admits of being traced in an interesting manner by intermediate steps. Deluc, soon after the discovery of the voltaic pile, contrived what he termed the *dry pile.* It may be constructed in the following manner:—Take a number of sheets of paper, one

surface of which has been coated with gold or silver leaf, and paste upon the uncoated surface a sheet of zinc foil; when sufficiently dry, place several of these sheets of paper one over another, the zinc faces all being arranged in one direction; then cut out, with a punch, a number of circular disks, and arrange them, to the number of 2000 or upwards, in a glass tube, the diameter of which is rather greater than that of the circular disks of paper, taking care that all the zinc surfaces are in one direction, and all the silvered or gilt surfaces in the opposite direction. A pile analogous to Volta's will thus be obtained; and if these disks be pressed together and connected at each end with a metallic wire, such a pile will cause divergence of the leaves of the gold-leaf electroscope when one extremity of it is made to touch the cap of the instrument, whilst the other end is connected with the earth, either through the human body or by means of any other conductor. If the pile be reversed, and then presented to the still diverging electroscope, the leaves will first collapse, and will then immediately open with the opposite kind of electricity. Indeed, if the wires attached to the two extremities of the pile be bent round and made each to terminate in a small metallic disk, the two disks being placed at a distance of about an inch and a half (3 or 4 centimetres) from each other, care being taken to maintain their insulation, an insulated slip of gold-leaf, suspended midway between the two disks will oscillate backwards and forwards between them, if an impulse be first given to it towards either side:—suppose it to approach the positive plate, it acquires a positive charge; it is then repelled from the positive plate, but is attracted by the negative plate, when it gives up its positive charge and becomes negatively electrified, in which state it is again atractted by the positive plate; this alternate movement of the gold leaf will continue uninterruptedly for months or even years.* With a dry pile, which contained 20,000 pairs, or disks, of zinc and silver paper, sparks have been obtained, and a Leyden battery has been charged sufficiently to produce shocks. It is worthy of remark that these actions are produced in Deluc's column only when the paper contains that amount of moisture

* Bohnenberger has contrived an extremely sensitive electroscope, which depends upon a modification of this experiment. Midway between the two insulated terminating disks of Deluc's pile, he suspends a single strip of gold-leaf by a metallic wire from an insulated plate of metal; this gold-leaf, however, is not near enough to either disk to touch it. If a body with the feeblest electrical charge be made to touch the insulated plate, the gold-leaf becomes electric, and is attracted towards the oppositely electrified pole of the pile.

which is found in it under ordinary circumstances, and which is considerable, although it usually passes unnoticed. If the paper be artificially dried, the pile loses its activity, but again recovers its energy as the paper reabsorbs moisture from the air. Provided that the two extremities of the pile be insulated from each other, it will retain its activity unimpaired for years; but if the ends be permanently connected by means of a good conductor, the zinc becomes gradually oxidized, and the electrical effects disappear.

Zamboni obtains a more effective instrument by substituting finely-powdered black oxide of manganese for the gold or silver leaf. One surface of the paper is coated with zinc or tin-foil, and the coating of peroxide may be given to the other surface either by rubbing it on in a dry state, or by applying it in admixture with water to which a little honey has been added. The paper disks are arranged in a column, and are terminated at either extremity by a metallic plate. These metallic plates are made to compress the paper disks by means of ligatures of silk which pass from end to end of the pile and bind the disks firmly together: whilst effectual insulation is provided for by giving the pile a non-conducting coat of sulphur, which is easily applied by a momentary immersion of the whole instrument in a bath of melted sulphur.

(299) *Water Battery.*—It has been already stated (259) that even with a single pair of zinc and copper plates excited by dilute acid, polarization and electric tension may be proved to precede the voltaic current, although the experiment is one of considerable delicacy. These effects of tension are strikingly exhibited in the case of Deluc's pile; but they may be shown in a manner still more decided by employing a numerous series of alternations of zinc and copper, each of which need expose only a very small surface, and may be excited simply with distilled water. Such an arrangement or *water battery*, consisting of a thousand couples, produces, if insulated, and connected at each of its extremities with a gold-leaf electroscope, considerable divergence of the leaves of each instrument. Such a combination will communicate a charge to a Leyden battery: this charge, although it rises only to a small extent, may be renewed and discharged for an indefinite number of times in very rapid succession. The wire which is connected with the last zinc plate of this battery is negative, whilst that which is attached to the copper is positive.

Gassiot (*Phil. Trans.* 1844, 39) has given an account of a very powerful and carefully constructed water battery, from which

he obtained results of great interest. This battery was composed of 3520 pairs of copper and zinc plates, arranged in separate glass vessels, covered with a coating of lac varnish; the glass cells were supported on slips of glass thickly coated on both sides with shellac, and these glass plates were insulated on varnished oaken boards, each board being further insulated by resting on thick plates of glass similarly varnished. All these precautions were found by experience to be necessary in order to preserve the insulation. When the conducting wires of this battery were brought within $\frac{1}{50}$ of an inch ($0^{mm}\cdot5$) of each other, sparks were obtained, and when the wires were made to terminate in brass disks which were brought very near each other, a rapid succession of sparks was maintained, which on one occasion continued without interruption for five weeks. A permanent deflection of the galvanometer was obtained when this instrument was included in the circuit whilst the sparks were passing; under similar circumstances, paper moistened with potassic iodide and included in the circuit, speedily gave indications of the chemical decomposition of the iodide. The chemical effects produced by the water battery are, however, always feeble, but they are similar in kind and in direction to those which are obtained when acids are employed as the exciting liquid in the cells; and the principal effect that would be obtained if dilute acid were substituted for water in such a combination would be an increase in the quantity of electricity, by increasing the consumption of zinc and the chemical action in each cell in a given time. The tension of the charge would be increased by the change of the exciting liquid, in proportion as the electro-motive force of each cell was augmented when compared with the resistance offered by the liquid employed in charging the battery. Neither in the water battery nor in any other form of battery is the tension, as measured by its power of overcoming resistance to conduction, increased by increasing the size of the plates.

Messrs. Warren, De La Rue, and Hugo Müller (*Journ. Chem. Soc.* 1868 [2], vi. 488) have constructed a battery in which the elements consist of rods of zinc and chloride of silver in a solution of sodic chloride placed in test tubes closed by stoppers of paraffin, and carefully insulated. Experiments with 2000 of these cells were made in 1875 (*Proc. Roy. Soc.* 1875, xxiii. 356), with 5640 in 1876 (*Proc. Roy. Soc.* 1876, xxiv. 167), and the number is now increased to 8040 (*Proc. Roy. Soc.* 1876, xxv. 322). This enormous battery has sufficient tension to produce sparks $8\cdot5^{mm}$. (·348 inch) long in air at the ordinary pressure when the positive

electrode is a copper point, and the negative a copper disk. The authors find (*Proc. Roy. Soc.* 1876, xxiv. 167) that the length of the spark is proportional to the square of the number of cells, 600 cells having a striking distance of ·0033 inch; 1200 of ·0130 inch; 1800 of ·0345 inch; and 2400 of ·0535 inch. Calculating from the effect produced by 600 cells the theoretical lengths for 1200, 1800, and 2400 would be ·0132, ·0297, and ·0528 inch respectively, which very closely approximate to the experimental results. The 8040 cells should give theoretically sparks ·5925 inch long; but the difference between this and the experimental number is due to the fact that the cells are not quite uniform in construction, and some have been longer in use than others. 100,000 of these cells would give a spark 91·66 inches long, and a million, 9166 inches or 764 feet.

It thus appears, 1. That by voltaic arrangements electricity may be obtained, exactly similar to that developed by the common machine, in its effects of tension and in induction towards surrounding objects, in the polar character of its action, and in the opposite nature of the electricities accumulated at the extremities of the apparatus. 2. That the quantity of electricity obtained by voltaic action is almost immeasurably greater than that procured by friction; but that unless its tension be exalted by using a very numerous series, it does not pass so readily through non-conductors in the form of sparks as the electricity of the common machine. 3. That, on the other hand, by allowing the electricity of the machine to discharge itself gradually through very small masses of imperfect liquid conductors which are susceptible of electrolysis, true electrolytic action may be produced.

The identity of the two forces under these different degrees of tension no longer admits of question; in the voltaic action the quantity is great, but the tension is feeble; whilst in the electricity of the machine the reverse is the case, the tension is very high, whilst the quantity is extremely small.

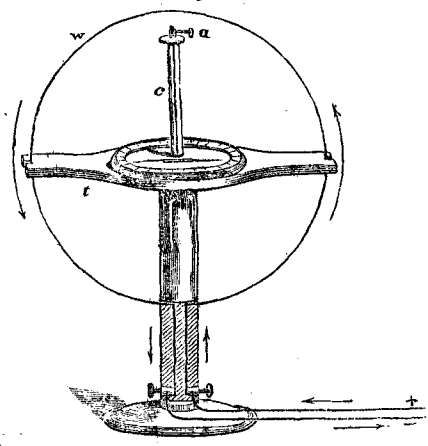
§ IV. Electro-Magnetism.

(300) *Law of Electro-Magnetic Action.*—The influence of an electric current upon a freely suspended magnetic needle has been already pointed out, but it will be needful to examine the nature of the connexion between magnetism and electricity somewhat more closely. Electricity in a state of rest has no influence upon a magnetized bar. It is only when the electricity is in motion that this magnetic action is excited. It has already been

explained (253) that the direction in which the magnetic needle is deflected depends upon the direction of the current; and it has been stated that when the needle points north and south, and a wire is placed parallel to the needle, if the current flow from south to north above the needle, the north end of the needle will move westward. The power which the wire exerts upon the needle varies directly as the quantity of electricity which traverses the wire: and when the current passes through a straight wire of considerable length (so that it may be regarded as infinite in relation to the needle) the effect upon the needle varies inversely as the distance of the wire from such needle.

(301) *Tangent Galvanometer.*—For measuring the strength of the current, galvanometers of various forms have been employed. When the strength is extremely feeble, the astatic galvanometer (fig. 207), is well adapted to the purpose, but in this form the value of the angular deviation requires to be experimentally determined for each instrument. When the current has a greater strength than can be conveniently estimated by the astatic combination, the *tangent galvanometer* is frequently employed. This instrument is simple, both in construction and in principle. The conductor, *w*, fig. 238, which is used for conveying the current round the needle, consists of a single coil of thick copper wire, bent into a circle of about 30 centimetres, or one foot in diameter. It is supported vertically in a small table *t*; the extremities of the wire being connected by means of binding-screws with the wires from the battery. Within the circle, *w*, a magnetic needle about an inch, or $25^{mm.}$ long, is suspended by fibres of unspun silk, *c*, horizontally over a copper plate graduated to degrees. In order to enable the movements of the needle to admit of more accurate measurement, its apparent length is increased by fastening a piece of fine copper wire to each end. This arrangement is protected from currents of air by means of a glass shade. The point of suspension of the needle is made to coincide accurately with the centre of the circle formed by the

Fig. 238.

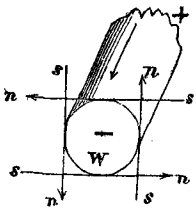


conducting wire: at *a* is a screw for raising or lowering the needle. When the coil of the instrument is placed with its plane exactly in that of the magnetic meridian, the needle, under the influence of the directive action of the earth's magnetism, assumes a position parallel to the plane of the circle. On transmitting the current through the wire, the needle receives an impulse which, if it were free from the inductive action of the earth, would place it exactly at right angles to the coil: owing, however, to the influence of the earth, the needle is unable ever really to assume this position; but it takes one which represents the resultant of the two forces, and as the action of the earth may be assumed to be uniform, the measurement of the angle enables the strength of the current which produces the deviation to be calculated. It may be demonstrated that the strength of the current is proportioned to the tangent of the angle of deviation. The instrument cannot be relied on for angular deviations which much exceed 70°, owing to the rapidly diminishing angular deviation produced by equal increments in the strength of the current when the deflection has reached this extent; but for all currents which produce a deviation of smaller amount, it affords a convenient measure. Other forms of galvanometer have been contrived, which it will not be necessary to describe in this work.

(302) *Influence of a Conducting Wire in exciting Magnetism.*—The action of the conducting wire upon the magnetic needle is not interfered with by interposing a sheet of glass or other insulator of electricity; and the magnetic influence is equally transmitted, although a sheet of copper, of lead, or of any other non-magnetic metallic conductor of electricity be introduced between the needle and the wire. The electric current, however, produces no divergence of the leaves of an electroscope which is brought into its vicinity. Not only does a wire which is conveying electricity affect a needle which has been already magnetized, but the conducting wire itself, so long as it is transmitting the electric current, displays magnetic properties. If a thin wire of copper, or of any other non-magnetic metal, be employed to complete the voltaic circuit, such a wire will, for the time, attract iron filings: and the filings will be arranged in a layer of uniform thickness around the whole circumference of the wire, and along its whole length. The moment that the connexion of the battery is broken, the magnetism ceases, and the filings fall off; but the attraction may be again instantly renewed on completing the circuit. The iron filings in this case become magnets, the poles of which are

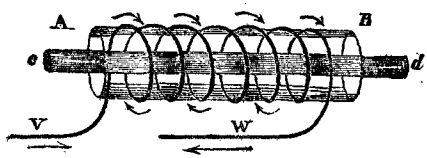
arranged alternately north and south around the wire. This arrangement may be better understood by reference to fig. 239, in which if w be supposed to represent a section of the wire which is transmitting a current from + to −, the north end of each fragment of iron would be arranged as represented by the points, *n*, *n*, of the arrows. If short wires of soft iron be placed in the direction of the arrows around the wire, they become temporary magnets, the north and south ends of which are indicated by the letters *n* and *s*. If pieces of steel be substituted for soft iron, they become permanently magnetic; all those which are above the wire, if the current be passing in the direction shown in the figure, will have their north ends to the left, whilst in all those below, the north ends will be to the right.

Fig. 239.



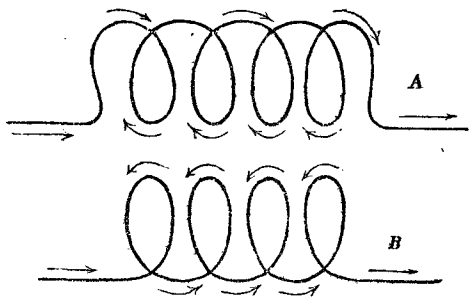
(303) *Formation of Electro-Magnets.*—We see, then, that every part of the wire along which a current is passing is magnetic. By coiling the conducting wire into a ring, a larger number of particles is brought to act upon a piece of soft iron, which is passed through the axis of the ring at right angles to the plane in which it lies; and by coiling up the wire into a helical form, without allowing the contiguous turns to touch each other, and supporting them upon a glass tube, the action of a very considerable length of wire may be concentrated in a very effective manner upon the same piece of soft iron, placed as at *c*, *d*, fig. 240. Very powerful temporary magnets may thus be obtained. If the wire be covered with cotton, or, still better with silk, to insulate the coils from each other, the effects may be greatly augmented by winding a second series of coils upon the first, and a third upon the second, and so on, till six or seven layers of wire are coiled around the bar which is to be magnetized. A row of coils which follows the direction of a left-handed screw would neutralize the effect produced by the right-handed helix, unless the current were reversed in its direction as it passes through such a coil, as a glance at fig. 241 will show, where A represents a right-handed helix, B a left-handed helix: in the straight portions of the wire, the current, as indicated by the arrows, flows in the same direction in both: but it is reversed in

Fig. 240.



the helices. In preparing an electro-magnetic coil it is not necessary, however, that the wire be coiled in one direction only, if the wire be continuous; for instance, if the coils follow the direction of the thread of a right-handed screw in the first layer, as in A B, fig. 240, the wire in winding it backwards from B to A will be formed into a left-handed helix, but this is of no consequence, because the direction of the current is also reversed in this layer, being now from B to A, so that the effect of the reverse twist of the wire is neutralized: in fact, if the currents in the turns of wire are parallel, the kind of helix is a matter of indifference.

FIG. 241.



A helix through which an electric current is passing is powerfully magnetic: the two magnetisms accumulating at its opposite extremities. If the helix be supported with its axis in a vertical position, and a bar of soft iron be partially introduced within it, as soon as an electric current of sufficient strength is passed through the coils, the bar will start up, and will raise itself in mid-air nearly equidistant between the two extremities of the coil; the iron, by induction, becoming for the time a powerful magnet. The poles of the iron bar are the same as those of the helix by which its magnetism is produced.

The most powerful electro-magnets, however, are those in which the iron is bent into the form of a horse-shoe, and around which an insulating conducting wire is coiled in several layers, with due attention to the direction in which the coils are arranged. In this way magnets have been constructed which are able to sustain a weight exceeding that of a ton (1016 kilogr.). The magnetism developed in the soft iron, under the influence of the voltaic current, attains its maximum in a few moments. It ceases as quickly, when the contact of the wires with the battery is broken; and, by reversing the direction of the current, the magnetic polarity of the bar is instantly reversed.

(304) *Molecular Movements during the Magnetization of Bars.* —The production of magnetism in a bar of iron, and the cessation of magnetism, are both attended with molecular motion,

which pervades the whole mass of iron. Joule (*Phil. Mag.* 1847, xxx. 76 and 225) has shown that the bar, on becoming magnetic, acquires a slight increase in length, and suddenly contracts to its former dimensions when the magnetism ceases, the elongation of the bar being proportional to the square of the intensity of the magnetism developed within it. It has been observed by Guillemin that if an iron bar be supported at one end so as to bend by its own weight, it becomes straightened to a greater or less extent when magnetised. Wertheim has also observed that the co-efficient of the elasticity of both iron and steel is diminished by magnetization. Each time that the bar either becomes magnetic or loses its magnetism, a distinct sound is emitted, the note being similar to that elicited by striking one end of the bar so as to produce vibrations in a longitudinal direction. The molecular movements, if repeated in quick succession by rapidly making and breaking contact between the ends of the helix and the wires of the battery, so as repeatedly and quickly to magnetize and demagnetize the bar, produce an elevation of temperature, which, as Grove has shown, is quite independent of the heat produced in the conducting wire by the current. In connexion with these molecular movements, it may be noted that Wiedemann finds when a current is transmitted along the axis of a magnet, the magnet suffers a slight degree of twisting. Gore (*Phil. Trans.* 1874, 529) has investigated the effect of passing a current through a piece of iron wire about 2½ metres long, hanging vertically, and magnetized by a helix of copper wire surrounding it. When the current passes along the wire from the south-seeking to the north-seeking end, a right-handed torsion results; and when either the current or the magnetization is reversed, the torsion is left-handed. A similar effect was observed with a bar of nickel, but no motion was observed with platinum, silver, copper, lead, tin, cadmium, zinc, magnesium, aluminium, brass, or German silver. A stretched cord of gutta-percha showed no signs of torsion when placed within the helix.

(305) *Laws of Electro-Magnetism.*—According to the researches of Lenz and Jacobi (*Pogg. Ann.* 1839, xlvii. 225, and 1844, lxi. 254) it appears that if the battery current be maintained of a uniform strength—1. That the magnetism which is induced in any given bar of soft iron is directly proportioned to the number of coils which act upon the bar: it is a matter of indifference whether the coils be uniformly distributed over the whole length of the bar, or whether they be accumulated towards its two extremities. 2. That the diameter of the coils which surround

the bar of small diameter scarcely influences the result, provided that the current be in all cases of uniform strength; for although the inductive influence decreases as the distance of the magnet from the wire, the induction produced by the increased length of the wire in the circumference of the coil is augmented in precisely the same ratio. 3. That the thickness of the wire composing the coil does not influence its effect upon the bar. 4. That the intensity of the magnetism is, *cæteris paribus*, proportioned to the strength of the current, being directly as the electro-motive force and inversely as the resistance of the circuit.* 5. That the *retentive* power of the magnet, like the attractive power in electricity, increases as the square of the intensity of the magnetism. 6. That the intensity of the magnetism induced upon a solid bar by a given current is proportioned to the surface which the bar exposes; or in cylindrical bars it is as the square root of the weight.† Bundles of isolated wires expose a larger surface than a solid bar, and hence they are susceptible of a higher amount of magnetism than a solid bar of equal weight. 7. That the employment of long bars has no other advantage over the use of short bars than that of removing to a greater distance the counteracting influence of the two magnetic poles upon each other.

According to Du Moncel the larger the armature, until it equals the electro-magnet in size, the more powerfully is it attracted.

The practical question in preparing an electro-magnet resolves itself into the determination of the thickness and length of the wires which are required to produce the *maximum* effect. It is obvious, that for a battery of a given power, the longer the wire which is employed, the greater is the resistance introduced, so that practically the number of convolutions has a limit beyond which nothing is gained by increasing them, and this limit is attained when the increased resistance introduced by the increasing length of the wire balances the gain produced by the influence of

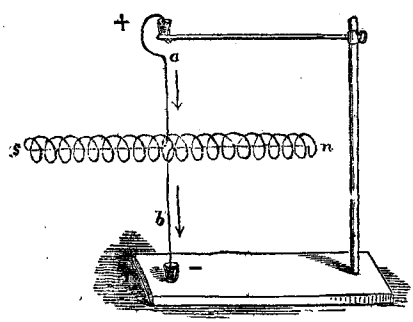
* This increase, it must be observed, only occurs up to a certain point, as there is a limit to the amount of magnetism which can be developed in iron, although the electricity may be indefinitely increased.

† Dub (*Pogg. Ann.* 1858, civ. 234), however, confirms the observation of Müller, which gives a different result—viz., that the intensity of the magnetism in cylindrical bars is, for equal currents in coils of equal number, proportioned to the square root of the diameter of the bar; the magnetism developed in a bar 10 centimetres thick being twice as intense as that produced in a bar of $2\cdot^{cm}\cdot 5$ in thickness; so that the *retentive* power is directly proportioned to the diameter of the bars.

the additional coils upon the bar; the greater the diameter of the coil the longer, of course, will be the wire required to form it, and the greater will be the resistance of such a coil in proportion to its magnetizing power. Experience shows, that in order to attain the most economical combination in the battery in proportion to the quantity of materials consumed, when magnetic power is required, the same rule must be followed as when chemical resistance has to be overcome—viz., that that combination is the most effective in which the resistance of the wires and of the coils which are exterior to the battery is equal to the resistance of the liquids and other materials used in the construction of the battery itself, or when in Ohm's Formula ($\frac{n\,E}{n\,R+r}=A$) the value of A most nearly approaches 0·5; in which case $r=nR$.

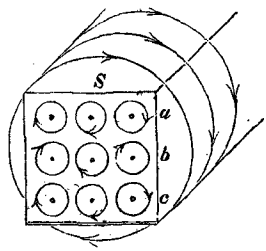
(306) *Ampère's Theory of Electro-Magnetism.*—It will be necessary to examine somewhat further the properties of a helical wire which is conveying a current, in order that the reader may be enabled to understand the theory of Ampère, by which he accounted for the mutual action of magnets and electric currents. If a simple helix, which for lightness may be made of thin wire, be freely suspended, it will, whilst conveying the current, place itself in the magnetic meridian; that is to say, it will point north and south, and will be attracted and repelled by a magnet which is presented to it, just as an ordinary bar-magnet would be. Fig. 242 shows a method of suspending the helix, or *electro-dynamic cylinder, n s*, so as to exhibit these effects; the wire, *a*, terminates in a small hook, which dips into a cup containing mercury, and this is connected with one of the wires from a small voltaic battery; the other end, *b*, of the coil dips into a second mercury cup, which is in communication with the other wire of the battery: the magnetism corresponding with that of the north end of the needle accumulates at one extremity of the coil, whilst the opposite magnetism accumulates at the other extremity: this effect necessarily follows from the influence of each coil upon its neighbours, since the north side of every coil is in one direction, whilst the south side is in the opposite. Ampère, who first pointed out the remarkable analogy between an ordinary magnet

FIG. 242.



and the helix when conveying an electric current, deduced from it a theory of the connexion between magnetism and electricity which has satisfied, hitherto, the rigorous requirements of mathematical analysis, and has also explained all the phenomena of electro-magnetism that have as yet been discovered. Ampère assumes that all bodies which exhibit magnetic polarity, derive this polarity from currents of electricity which are perpetually circulating around the particles of which the magnetic bodies are composed. Around each particle an electric current is supposed continually to circulate; the direction of these currents is conceived to be uniform, each current circulating in a plane at right angles to the magnetic axis of the particle. In fig. 243, the currents are shown as at *a*, *b*, *c*, circulating in a uniform direction around the particles of a bar magnet, of which the south pole, s, is nearest the observer. The resultant effect of these united and concordant small currents would be equivalent to that produced by a single current winding in a helical direction uniformly around the bar which would occupy the axis of such a helix. In an ordinary magnetic needle which is pointing north and south, currents would ascend on the western side and descend on the eastern. So that if the south pole is towards the observer, the direction of the current required to produce the magnetism will be the same as that of the hands of a watch with its face upwards. No definite proof of the existence of these currents can be given, nor can a reason for the persistence of such currents in permanent magnets be assigned; but granting that such currents do exist, all the mutual actions, between wires which convey currents, and permanent magnets, follow as a matter of necessity.

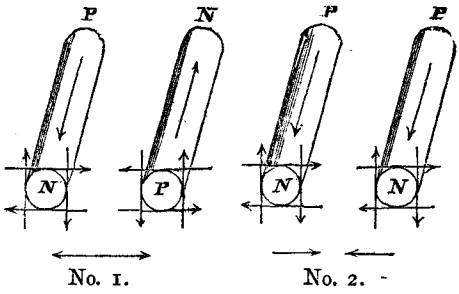
FIG. 243.



(307) *Mutual Influence of Wires which are conveying Currents.* —We proceed to point out one or two of these consequences. When two wires are freely suspended near each other, and electrical currents are passed through them, the wires will be mutually repulsive if the currents pass in opposite directions, but they will attract each other if the currents be in the same direction. Fig. 244 will explain the reason. When the currents are in opposite directions (No. 1), the magnetism on the inner side of the first wire is exactly similar to that on the contiguous side of the second wire, as indicated by the arrows arranged round P and N. The two north poles and the two south poles consequently

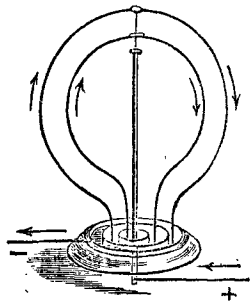
repel each other; whereas when the current is passing through the two wires in the same direction, as shown in No. 2, the effects are exactly reversed; attraction follows, and if the wires

Fig. 244.



No. 1. No. 2.

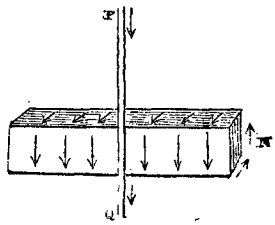
Fig. 245.



be freely suspended, as in Snow Harris's arrangement, represented in fig. 245, they will place themselves parallel to each other. Three concentric troughs containing mercury are arranged on a small stand; the current passes from one of the wires of the battery to the central trough, returns by the inner loop of wire to the second trough, and by the outer loop is transmitted to the exterior trough, which is in communication with the other wire from the battery. This attraction between currents which are passing in the same direction may be rendered evident in the contiguous coils of a helix: from this cause, a helix formed of a slender harpsichord wire shortens itself when the current is transmitted, but recovers its former dimensions when the current is intermitted; by suspending such a helix with its lower end dipping in a mercury cup, and passing a current through it, the shortening of the wire will raise the point, thus breaking the circuit, whereupon the attraction between the turns of wire ceases, and contact is again made. In this way alternate shortening and lengthening of the helix will take place as long as contact with the battery is continued. Now if it be granted that in every bar-magnet electrical currents are perpetually circulating around the particles of which it is composed, in a direction at right angles to a line joining the magnetic poles, we have in the foregoing experiments an explanation of the tendency of a magnet to place itself across a wire which is conveying an electric current, since, by such a movement, the currents in the magnet and in the wire assume a direction parallel to each other. Let P Q (fig. 246), represent a

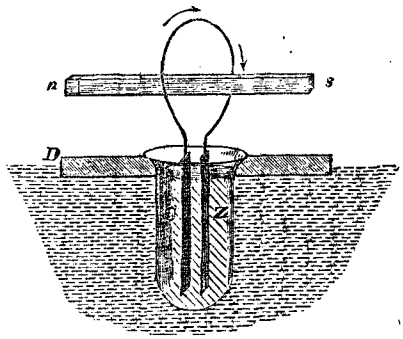
wire conveying an electric current in the direction of the arrows; N will indicate the north end of a magnet in which the current supposed to circulate around its particles would be parallel to the current in the wire P Q.

FIG. 246.



If the magnet be stationary whilst the wire is moveable, the wire will place itself at right angles to the magnet. In fig. 247, a plate of zinc, Z, is represented as connected by a loop of wire with the copper plate C; both are suspended in a tube containing diluted acid, and the little battery is made to float in a vessel of water by the aid of a piece of cork, D. If the north end of a magnet, *n*, be presented towards the loop in the direction shown in the cut, the wire will be attracted, and will place itself midway between the two extremities of the magnet; but if the south end be presented, the wire will be repelled; the little floating combination will turn half round so as to reverse its direction, and then will be attracted.

FIG. 247.



Motion is also produced in a wire which conveys a current, if it be suspended perpendicularly between the two poles of a horse-shoe magnet placed upon its side, the lower extremity of the wire dipping into a trough of mercury connected with one electrode of the battery, whilst it rests by a hook at its upper end upon a metallic arm which is in communication with the other electrode; according to the direction in which the current is passing, the suspended wire will be either attracted or repelled by the simultaneous action of the two poles of the magnet on the opposite magnetism of the two sides of the wire; the lower end will be thrown out of the trough of mercury; this movement will break the connexion with the battery, and the wire will then cease to be acted upon by the magnet until it falls back again into the mercury; the battery contact is by this means renewed, and the same series of motions is repeated. A spur wheel or star, if substituted for the wire, may in this manner be kept in continuous revolution;

for as one radius is thrown out, another enters the mercury, and thus renews the connexion with the battery, till it in its turn makes way for another.

(308) *Electro-Magnetic Rotations.*—The movements just described are not the only ones which the magnet and the wire produce on each other. If the action of the electric current be limited to a single pole of the magnet, a continuous rotation of the pole round the conducting wire may be obtained; or if the magnet be fixed whilst the wire is moveable, the wire will revolve around the magnet.

Faraday, by whom these rotations were first investigated, was led to their discovery by observing the manner in which a voltaic current acts upon a magnetic needle which is moved in its vicinity. If the conducting wire be placed perpendicularly, and a needle poised horizontally at its centre be made gradually to approach the wire on one side, each pole of the needle is first attracted, and on continuing the movement across the wire, is then repelled by the wire; on the other side of the wire the needle is repelled where it was previously attracted. The points indicated in fig. 248 by the letters A A, represent the positions of the wire when it produced attraction; R R, those in which it occasioned repulsion: at the points S and N midway between A and R, the needle is neither attracted nor repelled. From these results Faraday concluded that each pole has a tendency to revolve round the wire, and therefore that the wire has a similar tendency to revolve round the poles; the revolution of the north end of the needle, it was expected, would be in a direction the reverse of that assumed by the south end. Experiment completely verified these expectations. The facts admit of being shown in a variety of forms.

Fig. 248.

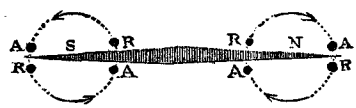
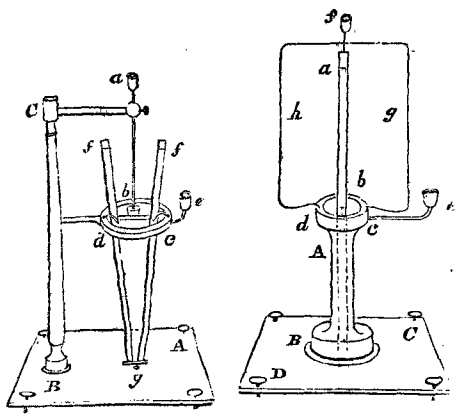


Fig. 249.



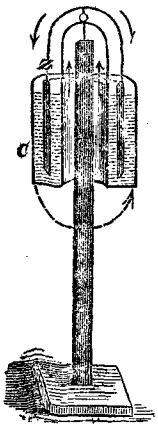
No. 1, fig. 249, shows an arrangement by which the magnet may be made

to revolve around the fixed wire, *a b*; *f f* are the north ends of two bar magnets, which are united below, and terminate in a pivot, *g*; this pivot works upon a hard steel plate in the board, A B; *c d* is a wooden ring which contains mercury, and is in metallic communication with the cup, *e*. At the centre of each of the magnets is a small brass hook which dips into the mercury of the trough, *c d*, for conveying the current transmitted through the wire, *a b*, which is supported by the arm, C. As soon as the connexion of the cups *a* and *e* is made with the battery, the magnet begins to rotate round the wire, *a b*, and continues to do so as long as the current passes; if the direction of the current be reversed, the direction of the rotation is reversed likewise. No. 2 is a similar arrangement for showing the rotation of the wire, *g h*, around the north end of the magnet, *a b*; the current enters at the cup, *f*, divides itself, and passes down *g* and *h* into the ring, *c d*, which contains mercury, and is supported above the board, C D, by the stand, A B: the circuit is completed by means of the cup, *e*: reversal of the current reverses the direction of the rotation. If the current descend in the wire around the north end of the magnet, the direction of the rotation is the same as that of the hands of a watch lying with the face upwards. The current may be passed through the upper half of the magnet itself, and if delicately poised, the bar may thus be made to rotate rapidly upon its own axis. These rotations may also be exhibited by liquid and by gaseous conductors; if the wires from a powerful voltaic battery be made to dip into mercury, the mercury over the point where the wires terminate will rotate rapidly if a magnet be held above or below the spot. The flame of the voltaic arc revolves with equal regularity and distinctness under magnetic influence; for instance, by making a powerful horse-shoe magnet a part of the circuit, and passing the current through the magnet itself, the voltaic arc of flame which may be drawn from one of its poles will rotate in the opposite direction to the flame which may be drawn from the other pole. This magnetic rotation of the electric discharge is also well exhibited when the induced current of Ruhmkorff's coil is passed through an exhausted globe immediately over the pole of an electro-magnet, the direction of the rotation being reversed with each reversal of the magnetism. (De La Rive, *Electricity*, 1856, ii. 248.)

A beautiful proof of the magnetic condition of the liquid part of the circuit so long as the current is passing, is exhibited by the rotation of the battery itself, in obedience to the action of a magnet. The experiment may be made as follows:—Let a double

cylinder of copper, shown in section at c, fig. 250, of about two inches (5 centimetres) in diameter and three inches (7·5 centimetres) high, be formed into a cell capable of containing liquid, and be supported by a point attached to a connecting strip of copper, over one end of a bar magnet; let a cylinder of zinc, z, be supported on a second point in metallic communication with the copper: as soon as a little dilute acid is poured into the cell, the zinc will begin to revolve around the magnet in one direction, whilst the copper rotates in the opposite; the current is ascending in the copper, whilst in the zinc it is descending around the same magnetic pole: round the north end of the magnet, the cylinder of zinc will move in the same direction as the hands of a watch which is lying with its face upwards.

Fig. 250.



Ampère has explained these rotations by means of the theory to which allusion has already been made; but it will not be needful to pursue this part of the subject further.

(309) *Electric Telegraph.*—The most important and remarkable of the uses which have been made of electricity, consists in its application to telegraphic purposes; an application which has not only brought distant towns upon the same island or continent within the means of instantaneous communication with each other, but which has spanned the seas, and placed an insular metropolis like London within momentary reach of the distant capitals of the Continent, of America, of India, and of Australia.

It would be impossible in a work like the present, to give even a sketch of the numberless modifications and improvements in the apparatus which have been suggested or practised for carrying out telegraphic communications by means of electricity, since the year 1837, which is memorable as the period at which Cooke and Wheatstone took out their first patent for electric telegraphing, and proved to the world the possibility of transmitting and receiving signals produced by electricity, with facility and with certainty, through insulated wires of great length. On the present occasion, an outline of the essential parts of the telegraphic system which is generally adopted in this country is all that can be attempted

The electric telegraph may be regarded as consisting of three parts—viz.: 1. The *battery,* or source of electric power. 2. The *line,* or the means of transmitting the signals.

3. The *telegraphic indicator*, or instrument for exhibiting the signals.

1. *The Battery.*—The apparatus for producing the signals is simply a voltaic battery, any form of which may be used; the one formerly in general use consists of a series of alternate pairs of copper and amalgamated zinc plates arranged in wooden troughs, subdivided into compartments, similar to those used with Smee's battery (fig. 221). These compartments, after the plates have been introduced, are filled with sand, which is then moistened with dilute sulphuric acid. In this form of instrument the risk of leakage is diminished and the amount of evaporation is lessened: the charge requires renewing once in ten days or a fortnight, according to the frequency with which the telegraph is used. Another form of battery which has been found to be effective for a long period consists of plates of amalgamated zinc, and gas coke, excited by solid mercuric sulphate moistened with water; the plates are arranged in compartments, similar to those used for the moistened sand. But modifications of Daniell's and Leclanché's batteries are now generally preferred to any other form.

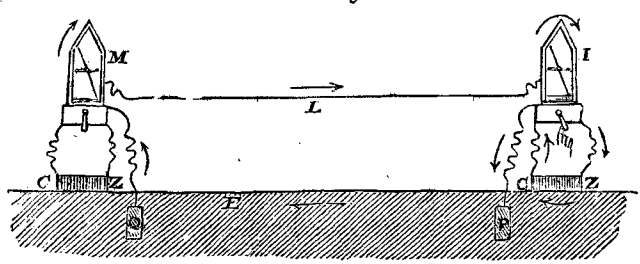
2. *The Line.*—The conducting wire was formerly made of copper, but is now generally made of iron wire about $8^{mm.}$ or one-third of an inch thick, coated with zinc to protect it from oxidation. For the purpose of insulation, this wire is supported upon wooden posts, which are firmly sunk into the earth, and which are kept dry at the upper extremity by means of a cap or case of wood fourteen or sixteen inches (35 or 40 centimetres) long, between the sides of which and the post is an interval of air. To the sides of this cap short tubes of porcelain, or supports of glass, are attached, and through these insulating tubes the wire passes. Suppose that a message is to be transmitted from London to Manchester; a continuous insulated conducting wire must extend between the instrument or battery in London and the instrument at Manchester which is to receive the signals, and there must also be a continuous conducting communication to complete the circuit between Manchester and London. This return conductor may consist of a second metallic wire which must be insulated from the earth and from the first wire, although it may be suspended upon the same posts side by side with the first. The earlier telegraph lines were all made in this way.

It was, however, discovered by Steinheil that the second metallic wire may be dispensed with, and that the earth itself may be employed as the conductor for completing the return communication between the two distant stations. The possibility of

doing this arises from the law of conduction in solids—viz., that the conductivity increases in proportion to the area of the section of the conductor. As a conductor of electricity, the earth is many thousand times inferior in power to any of the metals, if columns of each metal and of the earth of equal diameter be compared. But it is possible to multiply indefinitely the area of the conducting portion of the earth between the two stations, and thus a line of communication may be obtained which actually offers a far smaller amount of resistance than the metallic part of the circuit. In practice all that is found necessary, in order to take advantage of this conducting power of the earth, and to substitute it for the return wire of the telegraph, consists in leading a wire from the telegraphic apparatus at one end, into the earth, the wire being attached to a plate of copper which exposes a square metre or more of surface, this copper plate being buried in the ground, as represented at P (figs. 251, 252, 253). By increasing the size of this plate, any extent of surface of contact with the earth may be obtained, and thus, notwithstanding the intrinsic inferiority of the earth to the metals as regards its conductivity, the resistance which it offers, according to Breguet's experiments, is insignificant when compared with that of the telegraph wire itself. Another way of making an earth-plate is by soldering the return wire to the gas- or water-pipes of the telegraph office.

The general plan of this arrangement will be understood from fig. 251, in which M and I represent two telegraphic instruments,

FIG. 251.



one stationed, we will suppose, in Manchester, the other in London. L is the metallic line or wire of communication which connects the stations; E is the earth; and P, Q, copper plates attached to wires, one of which proceeds from each instrument. Suppose, for example, a message to be in the act of transmission from I, the instrument in London, to M, the instrument in Man-

chester. If c z represent the battery at the London station, the current will take the course indicated by the arrows: it will pass from c to a wire connected with the earth-plate, P, thence it will pass through the 200 miles of earth between the two cities; at Q it will be taken up again, and be transmitted by the wire to the instrument, M, thence it will be conveyed along the metallic wire, L, and back again to London, where it will pass through the instrument, I, and so return to the end, z, of the battery.

When it is impossible to insulate the conducting wire by supporting it in the air on posts, the whole length of the wire requires to be covered with an insulating material.* Caoutchouc and gutta-percha are found to be well adapted to this purpose. In this case, it is usual to substitute copper wires for the iron ones, as owing to the superior conductivity of copper, a wire of much smaller diameter can be employed without adding to the resistance, and a saving of space and of insulating material is thus effected, as well as a reduction in the inductive action, to which allusion will be made almost immediately. The wires, after having been covered with a coating of gutta-percha about $3^{mm.}$ or $\frac{1}{8}$ of an inch thick, may be enclosed either singly, or several of them side by side, in iron tubing, to protect them from mechanical injury: they are then placed under ground, in the same manner as pipes for the conveyance of gas or water. In the submarine telegraphs, copper wires coated with gutta-percha are carefully enveloped in tarred hemp, so as to form a compound rope, which contains several strands of conducting wire; the whole is protected by enclosing it in a flexible metallic covering, formed by carefully twisting several iron wires around the compound conducting rope already described: the exterior is often further protected by an outer covering of tarred hemp or other analogous material. The cable having been previously coiled up in the hold of a vessel, and one of its extremities having been properly secured upon the shore, is carefully lowered into the sea; from its weight, the electric rope at once sinks to the bottom as it is gradually paid out over the ship's side. When the

* The insulating power of different materials is very differently affected by temperature. It is always highest when the temperature is lowest. The insulating power of caoutchouc is diminished but slightly by a rise of temperature from 32° to 92° (33°·3 C.), whilst in gutta-percha the insulation is reduced more than half between the same points of temperature. It must be remembered that the effect of heat upon metallic conductors is exactly the reverse, a rise in temperature of copper from 32° to 92°, being attended with a diminution in its conductivity of nearly 10 per cent.

opposite shore is safely gained, the extremities of the conducting wire are connected on either side with other wires which are in communication with the telegraphic apparatus, and the signals can be at once transmitted. The increased pressure upon the gutta-percha, produced by submersion at great depths, is found to improve the insulating power of the material, the pressure upon each square inch being increased nearly 1 ton for each mile below the surface.*

In cases in which the wires are insulated with gutta-percha, and are then encased in iron tubes, or sunk beneath a body of water, it has been observed that if the wire be connected with the battery, the signal is not instantaneously transmitted to the opposite extremity; and that if the battery-contact be broken, there is not an instantaneous cessation of electric action at the distant point.

Faraday (*Phil. Mag.* 1854 [4], vii. 197) has shown that this retardation is produced by the inductive action of the current upon the gutta-percha insulator. The insulated wire, in fact, forms a Leyden jar; the gutta-percha is the dielectric; the wire within forms the inner coating, and the iron tube, or water of the ocean which surrounds it, forms the exterior coating. The time lost at first is that which is expended in giving to the gutta-percha its charge; and the current which is observed to continue for a short time after the wire has been disconnected with the battery, is produced by the gradual discharge of the electricity which had been communicated by lateral induction to the gutta-

* The most gigantic submarine cables which have yet been laid, are those which connect the coast of Valentia in Ireland, with Heart's Content, Newfoundland, a distance of 1670 nautical miles. There are three of these cables connecting the two hemispheres; one which, after the unsuccessful attempt in 1865, was successfully completed in 1866; the second, laid at one operation in 1866; and the third from the coast of France, laid in 1869. The cable of 1866 is 1858 knots in length, and is formed of a single copper conductor, consisting of seven strands of copper wire, of a diameter of 0·114 inch ($2^{mm}\cdot9$); this is enclosed in alternate layers of gutta-percha and "Chatterton's compound" (a mixture of gutta-percha with wood-tar, and resin), making a core of 0·464 inch ($11^{mm}\cdot78$) in diameter; this is covered with a serving of jute, soaked in infusion of catechu, and enclosed in ten bright steel wires, each protected with a covering of hemp; the whole forms a cable the entire diameter of which is 1·125 inch ($28^{mm}\cdot6$); its weight per knot in air is $35\frac{3}{4}$ cwt. and in water 14 cwt. (a knot = 6087 feet, or 2029 yards). The cable of 1866 loses half its charge in from 60 to 70 minutes. The total resistance of the 1858 knots of copper wire contained in this cable is equal to 7209 "British Association units" (note, p. 550).—(*North Brit. Review*, Dec. 1866.)

percha: the gutta-percha in this case becomes polarized, just in the same manner as the glass of an ordinary Leyden jar. If the conducting wire employed have a diameter of $\frac{1}{16}$ inch, a mile of such wire would expose a surface of 85·95 square feet; so that it is obvious that a cable, even of moderate length only, must be capable of acquiring an extremely powerful charge, as the amount of charge from a battery of uniform power is directly proportioned to the length of the wire. Variation in the degree of conductivity in the wire does not affect the amount of the charge by induction, but the amount of charge is very greatly influenced by the nature of the insulating material used. In the course of the experiments made by Wheatstone for the Government Commission on Electric Telegraphy, published in a report to the House of Commons, in 1860, it was found that the induction produced in gutta-percha was very much greater than that in caoutchouc; whichever material is employed, the amount of induction varies inversely as the square root of the thickness of the insulating envelope: so that the induction of a coating $\frac{3}{16}$ inch thick is only twice that of a coating $\frac{1}{16}$ inch thick.

Further, by increasing the diameter of the wire and the thickness of the covering in the same proportion, the amount of induction remains unaltered. A wire $\frac{1}{16}$ inch thick, covered with gutta-percha $\frac{3}{16}$ thick, experiences the same induction as a wire of $\frac{4}{16}$ inch coated with gutta-percha $\frac{3}{16}$ thick. The rate of transmission of the current in such coated conductors, when of uniform dimensions, is inversely as the square of their length (Sir W. Thomson).

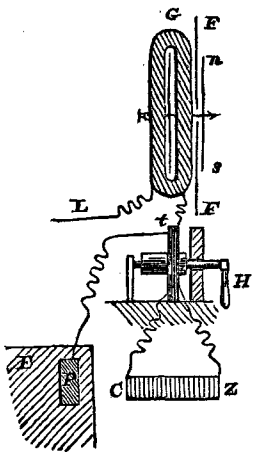
These observations do not affect the fundamental conclusions deduced from Ohm's law; in consequence of which it is found that the quantity of electricity transmitted is directly as the difference in its potential at the two ends of the wire; and from a source of uniform power, it is inversely as the length of the wire, but directly as the square of its diameter. When the wires are suspended in air, no retardation of this kind is observed; and no after-current is perceived. The gutta-percha in such a case cannot assume the polarized condition, owing to the absence of any conducting communication between its external surface and the earth by which the induced electricity could be carried off.

Supposing that the line of communication has been established, we have now to consider:—

3. *The Instrument for Exhibiting the Signals.*—The ordinary ndicator, or instrument by which the signals are exhibited, is

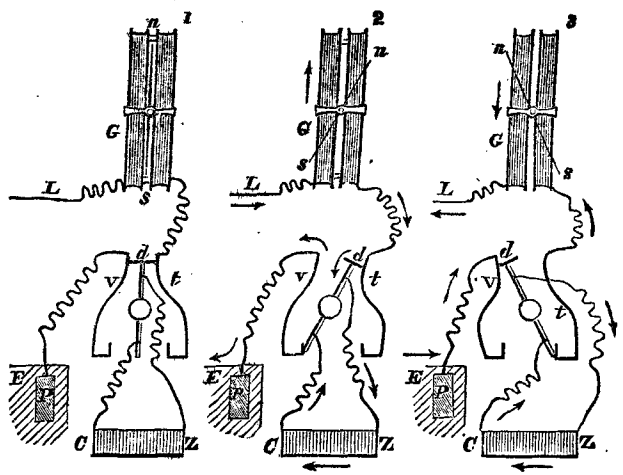
essentially a galvanometer, in which the astatic needles are suspended vertically, instead of being placed in a horizontal position. A side view of the coil is shown at G, fig. 252.

FIG. 252.



One of the needles is shown vertically suspended within it; the other needle, *n s*, is represented in front of the dial-plate, F, F, of the instrument. The needles are slightly heavier at their lower extremities than at their upper ones, in order that when disturbed from the vertical line, they may again resume it when the disturbing force ceases to act. The motions of the needle to the right or to the left are limited by a little ivory stud, which projects on either side from the face of the dial; loss of time, which would otherwise be occasioned by the unnecessary length of the oscillations of the needle, is thus prevented. L and P are the wires which communicate with the distant station; C Z is the battery; H is the handle by which the instrument is worked. Fig. 253 is intended to illustrate the principle upon which such

FIG. 253.



an instrument is made to exhibit the signals; the details of its construction have been slightly modified in the diagrams, in order that the course of the electric current may be more clearly traced.

No. 1 represents a back view of the essential parts of the instrument, when at rest and in a position to receive a message from the distant extremity. In this position, supposing the current to originate from the distant battery, and to enter the galvanometer G by the wire L, it will pass through the coil, will make its exit by the wire upon the right hand, which is attached to the metallic spring *t*; thence it will pass along the brass crosspiece, *d*, into the metallic spring, V, and complete the circuit through the wire attached to the plate, P, and the earth, E, by which it is returned to the distant station. The battery shown at C Z is inactive during the whole of this stage; the wires which proceed from its two extremities are attached to insulated pieces of brass at either end of the vertical piece which is connected with *d*. No current therefore can, in this position, be transmitted from this battery, since the wire proceeding from C is completely insulated. But suppose it be desired to transmit a signal from this instrument to the distant station:—by means of the handle, H (fig. 252), the piece to which *d* is attached can be pressed against one of the springs at *t* (fig. 253, 2), whilst its lower extremity, by the same movement, is pressed against the other spring, V; the current now passes from the battery in the direction shown by the arrows. From C it proceeds to V, thence, through the wire attached to P, into the earth; then through the distant station, where the instrument is arranged for receiving the signal, as in No. 1, and it then produces a deflection of its needle. Thence the current returns by L to the galvanometer coil, G, and then deflects the needle, returns through the wire attached to the spring, *t*, and by the metallic piece, *d*, completes the circuit through the wire attached to Z.

It is obvious that by reversing the movement given to the handle, H, the direction of the current and the motion of the needles in the coil will be reversed both in the near and in the distant instrument, as shown at No. 3. As soon as the operator has finished making his signals, the springs, V and *t*, restore the crosspiece, *d*, to the position shown in No. 1, and thus the instrument at once adjusts itself for receiving the signals from the distant station; the battery at C Z being thrown out of action, and the conducting communication with the line being restored through the crosspiece, *d*, by the self-acting power of the instrument itself.

By this arrangement a corresponding motion of the needle is always produced at the same instant at both stations, so that both the giver and the receiver of the message perceive the signal.

Since the needle admits of being moved either to the right or to the left, it is clear that by combining together on a definite plan a certain number of these movements, any letter or word may be transmitted: for instance, two movements of the upper end of the needle to the right may show the letter *A*; three movements in the same direction the letter *B*; four might indicate *C*; one to the right and one to the left *D*: and so on.

By employing two or more needles in each instrument, a greater number and variety of signals can be transmitted in the same time, but each needle requires a separate conducting wire, although the number of batteries need not be increased.

§ V. MAGNETO-ELECTRICITY.

(310) *Volta-Electric Induction.*—The term *volta-electric induction* was given by Faraday to the production of secondary currents, or currents in closed wires obtained by inductive action from wires conveying currents in the vicinity of such closed circuits. The circumstances under which these currents are formed will be best understood by a description of an experiment. If a wire through which a voltaic current is passing be placed parallel to a second wire, the two extremities of which are connected with the ends of a sensitive galvanometer, no perceptible effect is produced in the second wire, so long as the current passes without interruption through the first wire; but if the current through the first wire (or *primary current*, as it may for the sake of distinction be termed) be suddenly stopped by interrupting the connexion with the battery, a *secondary current* of momentary duration is produced in the second wire, and this current is *direct*, that is to say, it is in the same direction as that in the battery wire. On again completing the communication between the first wire and the battery, a momentary current or wave of electricity again passes through the second wire, but it is now *inverse*, or in the opposite direction to the primary current.

These effects may be much increased, if instead of employing simple wires, the wires be coiled into the form of two concentric helices: the wire which is to convey the primary current, or primary coil, being placed in the axis of the coil for the secondary current, and the ends of the secondary coil being connected as before with the extremities of the galvanometer. Under these circumstances the needle will receive a powerful impulse at the moment the primary coil is connected with the battery, but after

a few oscillations the needle will return to its original position, notwithstanding that the current through the primary coil is maintained; the instant, however, that the primary coil is separated from its contact with the battery, a powerful momentary impulse, occasioned by a current through the secondary coil in a direction the reverse of the former, will be produced upon the galvanometer needle.

Similar effects are exhibited by causing the primary coil, whilst it is transmitting the battery current, suddenly to approach towards, or to recede from, the secondary coil which is in connexion with the galvanometer. During the approach of the coil, the secondary current is in the opposite direction to the primary one: but during the withdrawal of the coil, the secondary current is in the same direction as the primary current. If a small helix be substituted for the galvanometer in the secondary coil, a steel needle may be magnetized by the induction of these instantaneous currents, and the intensity of the magnetism thus induced is proportional to the intensity of the secondary current. By discharging a Leyden jar through a primary coil properly insulated, a secondary current may be obtained in the other helix, but in this case it is always in the same direction as the current produced on breaking contact with the battery.

(311) *Magneto-Electric Induction.*—Since electricity may be made to elicit magnetism, it seemed reasonable to expect that the converse operation of obtaining electricity by means of magnetism should likewise be practicable. After several fruitless attempts to solve this problem, Faraday succeeded in discovering the conditions necessary to ensure this result (*Phil. Trans.* 1832, 125). The following experiment will serve to illustrate these conditions. Let the extremities of a helix of copper wire be connected by means of wires several metres in length with the two ends of a galvanometer, so that the needles shall be beyond the direct influence of the magnetic bars to be employed. Motion of a permanent magnet across the coils of the helix instantly produces a current in the wire; if, for example, a bar magnet be introduced into the axis of the helix, an immediate deflection of the galvanometer needle is produced; but if the magnet be allowed to remain motionless within the helix, the needle after a few oscillations returns to its zero; the instant, however, that the magnet is withdrawn, the galvanometer needle is deflected to the same extent as before, but in the opposite direction. When the marked end of a magnetic bar is introduced into a right-handed helix, the current which is produced so passes through the coils

as to enter the helix at that extremity at which the magnet enters; so that the current under these circumstances moves in the opposite direction to that of the hands of a watch which is lying with its face upwards.

If a bar of soft iron be placed in the axis of the helix, no current is produced so long as it remains unmagnetized; but if the opposite poles of two bar magnets be presented one to each extremity of the soft iron, so as to render it temporarily magnetic by induction, a momentary current is produced whilst it is acquiring magnetism, and this current corresponds in direction with that which would be occasioned by introducing a bar magnet the poles of which correspond in direction with those of the temporary magnet.

In like manner when two concentric helices are arranged as in the experiment on volta-electric induction (310), and a bar of soft iron is placed in the axis of the primary coil, a much more powerful secondary current is obtained than when the two coils only are used; since the soft iron in acquiring and in losing magnetism produces a secondary current, which in each case coincides in direction with that induced by the primary coil alone. If a bar of copper be substituted for the iron bar or *core* in the primary coil, the current is not stronger than when the two coils alone are employed.

If, as Ampère supposes, a series of electric currents are perpetually circulating around the component particles of a bar magnet, in planes at right angles to the magnetic axis,—the motion of a magnet in the axis of a helix, the opposite extremities of which are in metallic communication with each other so as to form a closed circuit, must necessarily produce a current in such a helix; for the magnet corresponds to a helix through which an electric current is passing: experiment shows that the direction of the currents induced by the magnet is precisely such as would be required by Ampère's theory.

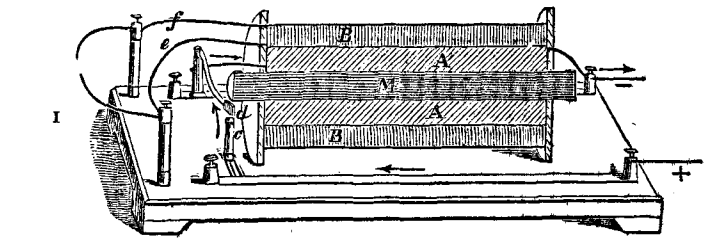
On making and breaking a circuit through a helix, an induced current is produced by the action of the contiguous portions of the coil on one another. This is called the *extra current,* and its production is readily detected by a simple experiment. The ends of the wires from a battery of 4 or 5 Grove's cells are placed in a vessel of mercury, and when the circuit is broken by raising one of the wires, a slight spark is observed at the surface of the mercury. If now a helix is introduced into the circuit, the spark produced on breaking the contact with the mercury will be much longer and brighter than in the previous case: the in-

duced current caused by the breaking of the current being in the same direction as the primary current, and of higher tension, is capable of passing across a longer interval of air than the primary current.

(312) *Ruhmkorff's Induction Coil.*—The secondary currents which are obtained by magnetic induction possess a high degree of intensity; if the circuit be broken at the moment that the current is passing, a brilliant spark will be observed at the point at which the interruption is occasioned.

An effective apparatus for exhibiting these secondary currents has been in use for several years, but it has recently been rendered still more efficient by Ruhmkorff. One of its forms is represented in fig. 254, in which No. 1 shows

FIG. 254.



a vertical section of the coil through its long axis, the other parts being shown in perspective. It consists mainly of two concentric helices of copper wire; the primary or inner coil, A A, consisting of a stouter and shorter wire than the secondary coil, B B, which is made of a very long thin wire, insulated by silk, and each layer of coils is carefully insulated from the adjacent layers:* M is a bundle of soft iron wire placed in the axis of the coils. At + and − are binding-screws for connecting the primary coil with a voltaic battery of three or four elements. This primary coil is not continuous throughout its length, but admits of being broken at *c* and *d*; *d* is a small armature of soft iron, to the under surface of which a plate of platinum is riveted, and the upper surface of *c* is also faced with platinum. So long as *c* and *d* touch each other, the current circulates uninterruptedly through A A: but as soon as the current passes through A A, the iron core, M, becomes magnetic and attracts *d*, consequently the contact between *c* and *d* is interrupted; the current immediately ceases to flow through A A, the magnetism in M disappears instantly, the hammer, *d*, falls, contact with

* In Ruhmkorff's 25 centimetre or 10-inch coil the inner or primary wire is $2^{\cdot mm}\cdot 5$ thick and 40 metres long, 300 turns of wire being formed upon the instrument. The outer or secondary coil is $0^{\cdot mm}\cdot 333$ thick, and 8000 metres (about 5 miles) in length, distributed in 25,000 coils.

c and with the battery is immediately renewed, *d* is attracted again, and it immediately falls back upon *c*.* Thus the battery itself acts as a means of making and breaking the contact several hundred times in a minute. A powerful current is induced in the secondary coil, B B, by each of these momentary currents in A A. In this instrument the secondary current is always transmitted in one direction only, the induced current on breaking contact being the only one which has sufficient intensity to traverse the coil. No. 2 shows an end view of the coil, and exhibits more distinctly the parts by which the contact is made and broken. The same letters apply in both cases. The shocks are of such intensity as to be very painful and often dangerous, even though experienced only for an instant. A continuous stream of sparks will pass between the insulated ends of the secondary wire, *e f*.

When a Leyden jar is connected with the terminals of the secondary coil, the outer end of the coil being attached to the inner coating of the jar, the noise and brilliancy of the spark is much increased. If the coil be excited by an increased number of cells, an advantage is obtained until a certain limit is reached; if this be exceeded, a powerful spark appears at the point of interruption of the primary coil, and the platinum surfaces are rapidly destroyed; but by now introducing a second Leyden jar into the secondary circuit, the brilliancy of the secondary spark is increased, and the spark at the contact-breaker nearly disappears. On again introducing an additional number of cells of the battery into the primary circuit, the brilliant spark at the contact-breaker reappears; but by the addition of a third Leyden jar the secondary discharge may be further increased in length and in brilliancy, whilst the excessive action at the contact-breaker is again diverted.

Faraday has contrasted the character of the spark, as it occurs before the introduction of the Leyden jar, with the appearance which it exhibits after the jar has been included in the circuit, by the following experiment:—

A platinum wire is supported across the knob of a Leyden jar, and its ends are brought near the platinum terminals of the secondary coil; two similar short interruptions in the secondary circuit are thus occasioned, and a noiseless spark of low luminosity passes across each interruption. If now the outer coating of the jar be connected by a wire with one terminal of the secondary coil, the spark on this side suddenly becomes brilliant and noisy, so that it is difficult to believe that in a given interval of time equal quantities of electricity traverse the interval between the two wires.

The noiseless spark kindles paper or other readily combustible objects, whilst the flash from the Leyden jar fails to kindle them. The difference between the two sparks is not in the quantity but in the duration of the spark; when the jar is used, a certain interval of time is expended in charging it by the current which moves comparatively slowly through the long secondary coil,

* Other improved forms of contact-breaker are now in use.

whilst the discharge occurs in a dense spark, the duration of which is imperceptible.

The power of the instrument may be much further increased by connecting the *primary* wire with a modification of the Leyden jar, which is commonly called a *condenser*: it consists of a band of brown paper, or, better, of oiled silk, or paper soaked in melted paraffin, on either side of which a sheet of tinfoil is pasted. 4 or 5 square metres (40 or 50 square feet) of coated surface are thus prepared and folded between two other bands of brown paper or of silk, and packed in a flat wooden case. The two coatings are connected with the binding-screws attached to *c* and *d* in the primary current.

The use of the condenser is to suppress the extra-current (311) which materially interferes with the action of the induction coil. From what has been already said, it is evident that the secondary current will be more powerful when the primary current is suddenly produced and suddenly interrupted; but since the extra-current is in the same direction as the primary, it will tend to maintain a flow through the primary wire after the contact has been broken by the electro-magnet; thus the strength of the current in the primary wire will fall gradually, and not suddenly, to zero. The condenser being connected with the primary wire on each side of the contact-breaker, cannot contain any charge while the contact is closed, the two sides of the condenser being connected by a metallic conductor of very little resistance; when, however, the contact is broken by the raising of the hammer, the extra-current which is formed, instead of leaping across the interval between the platinum studs, passes into the condenser: as the tension of the extra-current is higher than that of the battery, the condenser may be charged with a larger quantity of electricity than it would be capable of receiving from the battery alone. It then discharges itself through the only available passage—namely, the primary wire. This return current completely neutralizes any remainder of extra-current, and also deprives the soft iron core of its residual magnetism, much intensifying the current induced in the secondary wire.

The effect of the condenser is very remarkable in those instruments which are so arranged that the condenser may be connected or disconnected at pleasure. Without the condenser, the secondary current gives short and rapid sparks, whilst there is a succession of brilliant sparks produced by the extra-current between the platinum surfaces of the contact-breaker; when the condenser is connected, the secondary sparks are much longer,

and those at the contact-breaker almost entirely disappear. It does not increase the quantity of electricity in the secondary current, but it adds greatly to its intensity, and augments the striking distance, so that by its employment, and by increasing the dimensions of the coil, paying scrupulous attention to the insulation of the conducting wires, sparks of 450 or 500 millimetres (18 or 20 inches) in length, and of great intensity have been obtained. The intensity of this spark is also greatly increased by increasing the suddenness with which the continuity of the primary wire is broken. It is obvious that by this machine electricity of low tension may be rendered as intense as that from an ordinary plate-machine, whilst its quantity is much greater. An induction coil may indeed be substituted for an ordinary electrical machine in most cases, with great advantage, where a continuous discharge of sparks is required.

Dr. Robinson (*Proc. Roy. Soc.* 1866, xv. 171), states that the *quantity* of electricity obtainable with an induction coil increases with the diameter of the secondary wire up to $\frac{1}{6\cdot5}$ inch ($0^{mm}\cdot38$). Several coils may be combined so as to increase the quantity of electricity which they will furnish by connecting all their positive terminals together into one electrode, and all their negative terminals together, so as to form the other electrode; but no increase in the tension of the current will be thus obtained. When an increase in tension is desired, each secondary circuit must be connected in series so as to form one continuous circuit, each primary coil being excited by a separate battery.

In all cases where the terminals of the secondary coil are connected by a wire or other good conductor, there are two currents passing alternately in opposite directions through it: one produced each time that the contact of the primary coil is broken, and this is by far the most intense; whilst the other, produced at the moment of making contact, although equal in amount, is far less intense. Whenever the contact is broken, this latter current is intercepted, so that the discharges from the Leyden jar always occur in one direction only: and hence a Leyden jar or battery may be charged with the induction coil up to a certain degree far more rapidly than by an ordinary electrical machine.

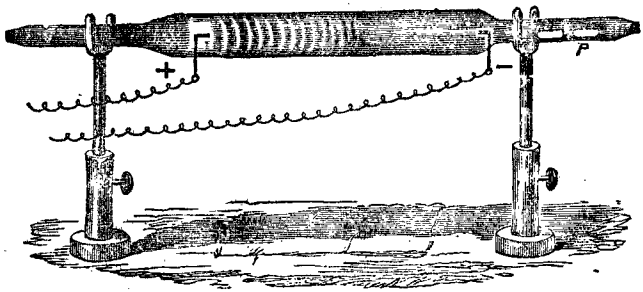
If the shadow of the spark obtained between the secondary wires of a Ruhmkorff's coil be thrown upon a screen by the intense light of the electric lamp, a cone of vapour will appear to issue from the point of each wire, due to the unequal refraction produced by the current of heated air; but the cone from the negative wire being more powerful, apparently beats back the

heated stream from the positive wire. These effects are the reverse of those produced in the ordinary voltaic arc, in which the greatest dispersion of matter and the highest temperature is observed to occur at the positive electrode (280). If the discharge of the secondary coil be allowed to occur in an exhausted receiver, the phenomenon of the auroral light is exhibited in a most beautiful manner through an interval of one or two metres. Gassiot has contrived a very striking modification of this experiment, by placing within the receiver of the air-pump a small tumbler or beaker lined with tinfoil about half way up the inside. The receiver should be open at the top for the admission of a sliding rod, which passes air-tight through a brass plate, ground to fit the top of the jar; the sliding rod is enclosed in a glass tube, open at bottom, and passes down to the inside of the tumbler and touches the metallic lining. On exhausting the receiver whilst the plate of the pump is connected with one terminal of the secondary coil, and the sliding rod with the other terminal, a beautiful and continuous cascade of electric light pours over the edge of the tumbler upon the metallic plate of the pump. The effect is heightened if the tumbler be made of a fluorescent material, such as uranium glass, and rests upon a glass dish washed over with quinine sulphate, the blue fluorescence of which contrasts well with the yellow of the uranium. If, instead of using the sort of Leyden jar employed in the foregoing experiment, this discharge be taken in an exhausted glass globe between two brass balls, it exhibits a very interesting appearance; the negative ball becomes covered with a quiet glow of light, whilst a pear-shaped luminous discharge takes place from the positive ball; between the two balls is a small interval nearer to the negative than to the positive ball, which is not luminous: when the exhaustion of the receiver is very perfect, the luminous portion is observed to be traversed by a series of dark bands or arches concentric with the positive ball; the presence of a little vapour of phosphorus renders these dark bands much more distinct. (Grove.)

The occurrence of these bands is as yet unexplained; but the attempts to trace them to their cause have led to numerous interesting investigations by Grove, who first observed them, by Robinson, and by others, but particularly by Gassiot, who has varied the experiment in numberless ways (*Phil. Trans.* 1858, 1, and 1859, 137). Gassiot's principal method of procedure has been to seal wires of platinum, and of other materials of various sizes and forms, into glass vessels or tubes. These tubes and vessels were subsequently exhausted more or less completely.

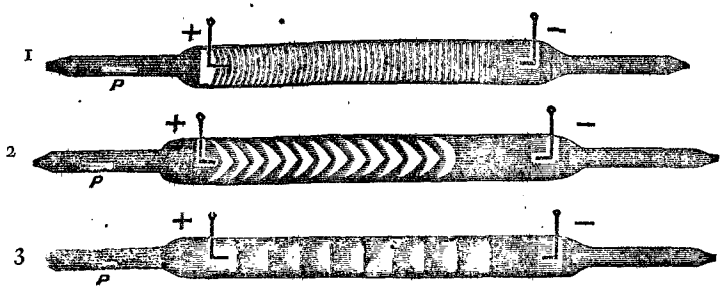
Various gaseous bodies were then introduced, and were afterwards more or less completely removed by the air-pump: effects of great variety and beauty were thus obtained. The general appearances may be thus described:—If a long wide glass tube (fig. 255) containing sticks of caustic potash, at P, be filled with

FIG. 255.



well-dried gaseous carbonic anhydride, and afterwards exhausted by the air-pump, the residual carbonic anhydride will be gradually absorbed by the caustic potash at P. The effects observed on connecting the wires +, −, with the secondary wires of the Ruhmkorff's coil, vary with the perfection of the vacuum. If the vacuum be merely that which can be obtained by an ordinary air-pump, no stratification is perceptible; a diffuse lambent light fills the tube: if the rarefaction be carried a step further, narrow striæ, like ruled lines, about $1^{mm}\cdot3$ in thickness, traverse the tube transversely to the line of the discharge, as shown in fig. 256, No. 1. A step further in the rarefaction increases the breadth of the bands, as seen in fig. 255; next the segments of light

FIG. 256.



assume a cup-shaped or conical form, fig. 256, No. 2; and by carrying the rarefaction still further, a series of luminous cylinders, of 25^{mm} or so in depth, with narrow dark lines between

them, are seen, fig. 256, No. 3. Finally, when the vacuum approaches perfection, there is neither discharge, light, nor conduction. Hence it would appear that the presence of material particles is absolutely necessary to the transfer of the electric current.

When the stratification is most distinctly visible, a dark space will always be observed near the negative pole, which, if of platinum, is seen to be covered with a bluish glow of light, within which, the wire, by an optical illusion, has the appearance of being red hot. Portions of the negative electrode are gradually thrown off in the form of fine metallic particles as the experiment is continued, and the wire rises considerably in temperature. The appearance of the stratification varies greatly with the modifications in form given to the wires. If the negative wire be enclosed within a capillary glass tube which is open, and projects beyond the wire for an eighth of an inch ($3^{mm.}$), or a little more, all the stratification disappears, and a jet of light escapes from the open end of the capillary tube, passing down the exhausted vessel.

These stratified bands and luminous discharges are powerfully affected by the magnet; if the negative wire be undermost in one of these exhausted tubes suspended vertically, and it be completely covered with a stratum of mercury, it will be found on causing one end of a magnet to approach the termination of the luminous bands in the direction of the axis of the tube, that the stratification will become modified, and will present an appearance resembling that which might be occasioned by stretching a spiral spring, supposing it were luminous; indeed, by suitable means, the discharge may, as De La Rive has shown, be made to rotate around the magnetic pole. Plücker has shown that the light from the negative pole is also especially affected by magnetism, the lines of light becoming parallel to the magnetic curves; and Gassiot has found that, by arranging a tube so as to cross the lines of magnetic force which emanate from the poles of a powerful electro-magnet, he can instantly arrest the luminous discharge by magnetizing the electro-magnet; but on breaking the connexion of the magnet with the battery, the discharge is immediately renewed. De La Rive and Sarasin have found that when a discharge in a rarefied gas is submitted to the action of a powerful magnet, the pressure of the gas is increased in the portion of the tube nearest to the magnet. (*Ann. Chim. Phys.* 1871 [4], xxii. 181.) Mr. Varley introduced into one end of an exhausted tube a small piece of talc supported on a fibre of silk. The tube contained

two loops of aluminium wire which were connected with a battery of about 350 cells: on passing the current the whole tube was filled with a luminous cloud, but when the tube was placed between the poles of a powerful magnet a luminous arch was formed, passing through the rings and ending near the walls of the tube. When the tube was placed in such a position that the luminous arch impinged on the piece of talc, the latter was repelled, no matter which way the current was passing (*Proc. Roy. Soc.* 1870, xix. 236). This is in accordance with the phenomena observed by De La Rive and Sarasin.

The phenomena above described have recently attracted a large share of the attention of electricians, from their intimate connexion with the mode in which electricty is propagated and transmitted from point to point.

The stratified light produced by Ruhmkorff's coil is, from the nature of the apparatus, intermittent, as may be very simply and beautifully shown by attaching one of the vacuum tubes to an axle which can be thrown into rapid rotation, the two arms of the tube moving like spokes of a wheel upon the extremity of the axle. In this arrangement, one extremity of the tube is maintained in unbroken contact with one extremity of the induction coil, whilst the other extremity is in like manner connected with the other end of the induction coil. As the rotation proceeds, if the experiment be made in a darkened room, the tube will be visible momentarily, several times during each rotation, and will produce the appearance of a star of light, each arm of the star exhibiting distinct stratified bands, and appearing to be stationary, owing to the briefness of the time for which it is visible.

It was supposed that these phenomena of stratification were connected with undulations produced by the rapidly succeeding currents of the induction coil. Gassiot, however, has shown that this is not the cause, by producing the stratified appearance from the discharge of a Leyden jar when somewhat prolonged by transmitting it through a portion of wet string; Quet and Séguin, by charging the jar feebly, have obtained similar effects without the use of the wet string. Gassiot also obtained them directly from the water battery of 3500 cells (299), as well as from a series of 400 carefully insulated small pairs of Grove's construction, on connecting each terminal of the battery with one of the insulated wires of the exhausted tube. A beautifully distinct stratified discharge was produced, which was not arrested by the introduction of a voltameter into the circuit. The quantity of electricity thus transmitted is so small that the amount of water decomposed

is barely perceptible. This is, therefore, not the true voltaic arc. On causing the terminals of the Grove's battery in the exhausted tube gradually to approach each other until within about $37^{mm.}$, the true voltaic arc was suddenly established, and an immense rise of temperature instantly occurred; but the interesting point of the experiment was, that the arc itself was seen to be distinctly stratified.

The passage of the electric spark through compound gases or vapours is attended with a partial separation of their components in the line of the discharge. But the experiments of Perrot (*Ann. Chim. Phys.* 1861 [3], lxi. 161) appear to have proved that the spark from Ruhmkorff's coil produces in addition a true electrolytic decomposition of the compound vapour. In the case of steam, for example, oxygen appears in larger quantity at the positive wire, and hydrogen in excess is collected at the negative; but a much larger quantity of the two gases is evolved than is due to true electrolysis. Long sparks, if transmitting equal amounts of electricity in equal times, were found to be more effectual in producing decomposition than small ones. In synthetic experiments on the combination of oxygen and nitrogen to produce nitric acid, it was found that long sparks also furnish a larger quantity of acid than shorter ones. If the length of the spark be increased in any given circuit, the gain increases only up to a certain point; the resistance offered by the length of the interposed stratum of air beyond this point diminishes the amount of electricity which circulates, to an extent which more than counterbalances the gain obtained by increasing the length of the spark.

The energy of the secondary induced current in effecting the combination or the decomposition of gases and vapours, is much greater than that of the ordinary cylinder or plate electrical machine. The interposition of a condenser in the induced circuit augments the intensity of the chemical action of the spark; but it decreases the number of sparks in a given time, so that if the spark possess sufficient intensity to pass, no gain in the amount of the body decomposed is effected by the use of the condenser.*

(313) *Inductive Action of Currents—Henry's Coils.*—When the connexion between the plates of a battery is made by means of a single, long, straight wire, a brilliant spark is seen at the moment that the contact with the battery is broken; but when the con-

* Full details of the numerous researches made by Quet and others with Ruhmkorff's coil will be found in Du Moncel's *Notice sur l'Appareil d'Induction Electrique de Ruhmkorff*, 4th edit.

nexion is made by means of a short wire, and contact is broken, only a very small spark is produced. When a long wire is employed, the same length of wire, if coiled into a helix, gives a much brighter spark than when it is used merely as a straight conductor. The brilliant spark which is observed when the long wire is used, is produced by the inductive action of the battery upon the electricity of the wire itself. The bright spark obtained from the battery wire on breaking contact arises from a current which is transmitted through the wire in the same direction as that from the battery itself. This inductive action may be entirely diverted, if a second helix, the ends of which are in metallic communication with each other, be placed either within the primary coil or exterior to it.

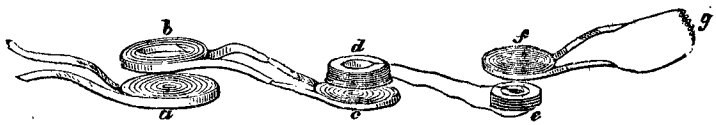
If the conducting wire be coiled into a helix within which an iron core is placed, the current on breaking contact acquires sufficient intensity to communicate a powerful shock, when the ends of the wire are grasped by the hand at the moment that the wire is disconnected with the battery, although the battery itself may be quite inadequate to produce any shock when its extremities are connected by a short wire. A striking experiment of this kind is related by Prof. Jos. Henry (*Phil. Mag.* 1840 [3], xvi. 200). A very small compound battery was formed of six pieces of copper bell-wire, each about an inch and a half (4 centimetres) long, and six pieces of zinc of the same size; the current which this arrangement produced was transmitted through a spool of copper wire covered with cotton: this wire was 5 miles (8046 metres) in length, and $\frac{1}{16}$ of an inch ($1^{mm}\cdot5$) in diameter, and it was wound upon a small axis of iron. The shock, on breaking the connexion with the little battery, was distinctly felt simultaneously by twenty-six persons who had formed a circle by joined hands, and who completed the circuit between the two ends of the wire. The shock which was felt on making contact with the battery was barely perceptible. A current is produced on making contact, but it is feeble, and in a direction the reverse of that emanating from the battery. Even a thermo-electric battery (317), if the current which it yields be passed through the coil, will furnish sparks on breaking contact.

Henry, in the paper above referred to, has made some interesting observations upon the action of the battery current in inducing secondary currents. He employed for transmitting the primary current a flat coil or ribbon of sheet copper about 93 feet (28·3 metres) long and $1\frac{1}{2}$ inch ($38^{mm}\cdot$) wide. This ribbon was sometimes coiled in the manner shown at *a*, fig. 257, sometimes

in the form of a ring as shown at *b*. This coil was combined under various circumstances with other similar coils, each about 60 feet (18 metres) long, or with helices of fine copper wire of various lengths. The form of ribbon is a very advantageous one, as it offers a large sectional area in the conductor, and thus diminishes the resistance, whilst the different layers of the coil are approximated to each other with the smallest possible intervals between them. When it was coiled as at *b*, and a helix placed within the ring so formed, each time that the current from the battery through the ribbon was interrupted, a secondary current of considerable intensity was obtained in the helix: the helix could be supported upon a plate of glass which rested upon the flat coil, and still the inductive action was obtained; but if a metallic plate were interposed between the coil and the helix, no secondary current was obtained in the helix, because it was transferred to the interposed conducting plate.

By arranging a series of coils in the manner represented in fig. 257, Henry succeeded in obtaining a succession of induced

FIG. 257.



currents by their mutual action. If *a* represent the coil in connexion with the battery, *b* and *c* are arranged to form a continuous coil, through which, by induction, a momentary current is produced each time that the connexion of the coil *a* with the battery is broken; the current in *b c* then being direct, or in the same direction as in *a*. Now if two wire helices be connected together and placed as at *d* and *e*, the induced current in *c* will produce a second induced current, or *current of the third order*, in *d e*; but this current will be in the opposite direction to that in *b c*. If *f* be a ribbon coil placed above *e*, with its ends united by a small helix at *g*, a third current, or *current of the fourth order*, will be obtained, but it will be in the opposite direction to that in *d e*. If these different currents be compared together, they will be in the direction following:—

a	primary current (on breaking)	
b, c,	secondary current . . .	direct
d, e,	current of the third order .	inverse
f, g,	current of the fourth order . .	direct.

By acting upon the principle just explained, and carefully insulating the coils, currents even of the seventh order have been obtained, the successive currents being alternately direct and inverse.

Similar currents of equal amount, but of lower tension, are obtained each time that the primary circuit is completed, but the direction of the currents in this case is reversed: so that on completing the primary circuit, the currents would be as follows:—

a	primary current (on making)	direct
b, c,	secondary	inverse
d, e,	tertiary	direct
f, g,	quaternary	inverse; and so on.

These effects are produced by a series of complicated actions which may be summed up as follows:—The primary current has the power of producing two induced secondary currents in opposite directions, one on making the other on breaking contact; these currents admit of being separated from each other. They are equal in amount, but the current on breaking contact has the highest tension, and will traverse the greater distance in the form of a spark. *Each* secondary current in *b c* may give rise to *two* opposite tertiary currents in *d e*, but these currents are separated by an interval of time too small to be appreciated, because the secondary current itself is instantaneous. These two tertiary currents are equal in quantity, but differ in tension; the tertiary current produced by the cessation of the secondary being the stronger. Again, each of these momentary tertiary currents is in its turn capable of developing in *f g* two opposite quaternary currents, equal in amount but differing in tension. At each interruption of the primary current, therefore, we have one instantaneous secondary current in *b c*, two tertiary in *d e*, and four quaternary in *f g*. If all these currents were equal in tension as well as equal in quantity, they would neutralize each other; but since their tension is not equal, a series of phenomena is produced, owing to the alternate predominance of the tension of the currents moving in one direction in one circuit, and in the opposite direction in the succeeding circuit.

Henry has shown that induced currents of several successive orders may also be obtained by the momentary passage of electricity occasioned by the discharge of the Leyden jar.

These induced currents not only give powerful shocks, but they magnetize steel bars and produce chemical decomposition.

The latter may be shown by interposing acidulated water or a solution of potassic iodide between platinum wires which are in connexion with the ends of the coil. It is easy to obtain either currents of high intensity such as those required to produce shocks, or currents of large quantity such as would be required for magnetizing steel, or for igniting platinum wire, by varying the diameter and length of the conductor. When a long thin wire was employed, as by uniting the two helices as at *d* and *e*, a current of great intensity, producing powerful shocks, was obtained; but this same current could be made to induce in the flat coil *f* a current of greater quantity, but of less intensity.

Owing to these variations in quantity and intensity, the investigation of the laws of such induced currents is complicated and difficult. Abria (*Ann. Chim. Phys.* 1841 [3], i. 385, and iii. 5) has published some careful researches upon them, but additional experiments are still needed.

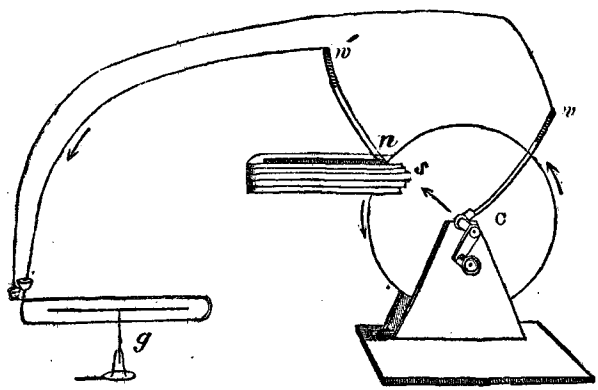
(314) *Arago's Rotations.*—A remarkable exemplification of the facility with which secondary currents are induced by magnetic influence, and of the mutual action of such induced currents, is exhibited by the following experiments of Arago. If a magnet be suspended freely by its centre in a horizontal direction, parallel to a circular disk of copper which can be made to rotate horizontally beneath the magnet, it will be found, if the centre of suspension for the magnet be directly over the axis of the rotating disk, that when the disk is made to revolve with a certain degree of velocity the magnet begins to rotate also in the same direction as the disk; and the more closely the disk and the magnet are approximated, the more rapid is the rotation, whilst at the same time a repulsive action is exerted upon the magnet in a direction perpendicular to the plane of the disk. This rotation occurs as freely when a sheet of paper or of glass is interposed between the magnet and the metallic disk, as when air only intervenes. Disks of other metals also produce this effect upon the magnet by their rotation, but none of them show it so readily as copper; the facility with which the effect is produced being directly as the power of the rotating disk to conduct electric currents. If a narrow strip be cut out of the metallic disk, extending from its circumference to the centre, no motion will be produced in the magnet when the disk is made to revolve; but if the cut edges of the divided disk be connected by soldering a piece of wire across the division, the rotation will be effected as readily as when the disk was entire. From causes similar to those which produce the foregoing results, it is found that if a

magnetic needle or a bar magnet be set vibrating parallel to the surface of a disk of copper, it will come to rest much more speedily than if vibrating over paper or glass.

These effects were first satisfactorily explained by Faraday; he found that whenever a piece of conducting matter is made to pass either before a single pole or between the opposite poles of a magnet so as to cut the magnetic curves at right angles, electrical currents are produced across the metal, transverse to the direction of motion.

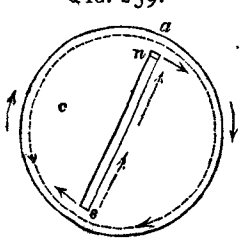
For example, let the copper disk, c, fig. 258, be made to revolve, in the direction of the arrows on the circumference, between the poles, *n s*, of a horse-

Fig. 258.



shoe magnet, and let a wire *w*, which is connected with one end of the galvanometer, *g*, be pressed against the centre of the disk, whilst the other wire *w'* from the galvanometer rests against the edge of the disk between the magnetic poles. Under these circumstances, a current will be found to flow from the centre towards the circumference of the disk, c, and then through the wires, as shown by the arrows. If the disk be made to revolve in the opposite direction, the current will flow from the circumference towards the centre of the disk. Currents may also be obtained from any of the forms of the apparatus which exhibit the rotation of magnets round a conducting wire, or of the wire round the magnet, if a galvanometer be substituted for the battery, and if the magnet or the wire be made to revolve by hand.

Fig. 259.

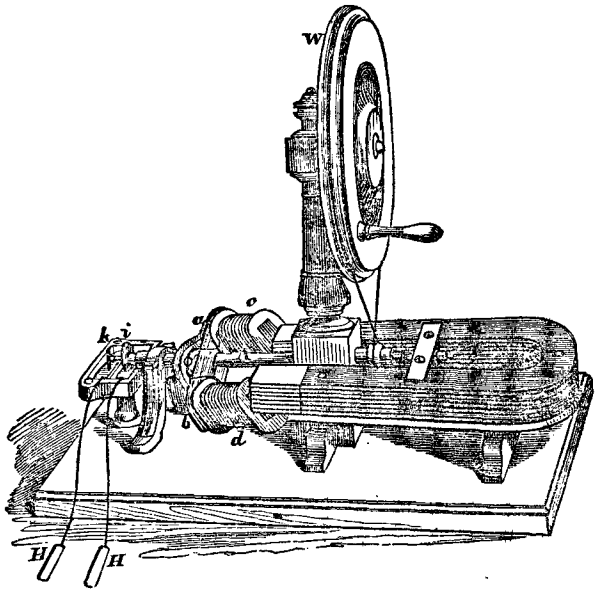


Now let us suppose that in Arago's experiment we are looking down upon the revolving disk, c, fig. 259; when the disk revolves beneath the magnet, it cuts the magnetic curves at right angles: currents are produced underneath the north pole, from the centre of the plate towards the circumference, *a*, beyond the pole. These currents occur in the opposite direction—viz., from the circumference to the centre, underneath the south pole, and thus traverse the diameter of the plate parallel to

the magnet, returning by the more distant parts of the plate, as shown by the dotted arrows. Such currents necessarily exert a repulsive action upon the magnet in a direction which coincides with that in which motion is observed, and no currents are obtained until either the magnet or the plate is set in motion.

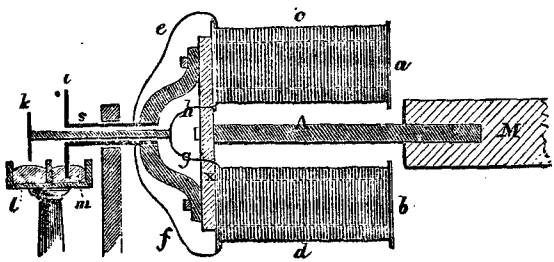
(315) *Magneto-Electric Machines.*—Various machines have been contrived for the production of magneto-electric currents; one of the most convenient of which is Saxton's magneto-electric machine. It is represented in fig. 260, in perspec-

FIG. 260.



tive; fig. 261 shows a section of the coils and armature on a larger scale. It consists of a powerful horse-shoe magnet, M, placed horizontally upon one of its sides: in front of its ends or poles, and as close to them as is possible without

FIG. 261.



producing actual contact, an armature of soft iron, *a b*, is made to revolve upon a horizontal axis, A, which admits of being turned by means of a strap passing over a multiplying wheel, W. This armature consists of two straight pieces of iron, about two inches (5 centimetres) in length, which, by means of a cross-

piece of iron, x, are connected together parallel to each other, at such a distance that they shall be opposite the middle of each pole of the horse-shoe magnet. Around each limb, *c d*, of the armature, a long fine copper wire, covered with silk to insulate the coils from each other, is wound in several successive layers. The corresponding ends of each of these helices are connected together; one pair, *e f*, is soldered to the spindle, *s*, on which the armature rotates, and through it is connected with a circular copper disk, *i*, the edge of which dips into a cup of mercury, *m*, whilst the other pair of wires, *g h*, is connected with a stout piece of copper which passes through the axis of the spindle, *s*, from which it is electrically insulated, and terminates in a slip of copper *k*, placed nearly at right angles to the crosspiece, x, which connects the two limbs of the soft iron armature. Beneath the slip of copper, *k*, is a second mercury cup, *l*, which can be made to communicate with the cup, *m*, either by a wire, or by some other conductor of the current. The arms of the slip, *k*, alternately dip into the mercury, and rise above it, and the points of contact are so arranged that the circuit (which, when *l* and *m* are properly connected, is complete so long as *k* is beneath the mercury) shall be broken at the time that the armature loses its magnetism. Under these circumstances a bright spark is obtained each time that the slip *k* quits the mercury. Four currents are therefore produced in the wire surrounding the armature during each complete revolution, two successive currents being in one direction, and the two others being in the opposite direction. Suppose, for example, that the limb, *c*, of the armature is opposite the marked pole of the steel magnet: if now it be made to recede from this pole, a current will be produced in a given direction through the coil which surrounds this limb, and on the approach of the same limb towards the unmarked end of the magnet, a second current will be produced in the same direction through the coil; a third current will be produced, but in a reversed direction, as the limb *c* leaves the unmarked end of the magnet, whilst a fourth current will be produced on the approach of the limb *c* to the marked pole of the magnet, and will coincide in direction with the third current. If the connexion between the mercury cups, *l* and *m*, be effected by grasping with the hands two copper cylinders, H, H, each of which by means of a wire is in connexion separately with one of the cups, a succession of powerful shocks will be experienced. Acidulated water and many saline solutions may be decomposed if these currents be transmitted through them; but in order to produce polar decomposition, it is necessary to suppress or turn up one of the points of the slip *k*, and thus to lose half the power of the machine: otherwise the currents at each half revolution are in opposite directions.

In the construction of these magneto-electric machines, great care must be taken that the insulation of the coil is very perfect. Different effects are obtained from such a machine by varying the length and the diameter of the wire which is wound around the armature. When currents of high tension are required, such as those needed for giving shocks, or for the decomposition of electrolytes, a great length of thin wire is preferable; but a much smaller length of thicker wire will give the largest sparks, and will ignite the greatest length of fine platinum wire. A machine upon this principle has been contrived by Wheatstone for exploding charges of gunpowder, when provided with Abel's magnet fuse, which seems to leave little to be desired in simplicity, certainty,

and facility of application. (*Report to Secretary for War*, Wheatstone and Abel, Nov. 1860.)

Wheatstone and others have contrived magneto-electric machines, by which a continuous electric current in a uniform direction may be kept up for any length of time. These batteries are, in fact, combinations of several simple machines, similar in principle to Saxton's; the coils are connected together so as to form a continuous circuit. The armatures are so arranged that each shall in turn become magnetic, just before the preceding armature has entirely lost its magnetism. By this contrivance, the current is made to commence in one coil before it has ceased in the coil which immediately precedes it.

Magneto-electric machines are now used in Birmingham on a large scale, as a substitute for the voltaic battery, in processes of electro-silvering and electro-gilding. A single Saxton's machine will, if kept in continuous revolution, precipitate from 90 to 140 ounces (2·5 to 4 kilogrammes) of silver per week from its solutions; and machines have been constructed by which 17 ounces or 0·48 kilogr. of silver per hour have been deposited upon articles properly prepared for this mode of plating.

Mr. Holmes has succeeded, by the use of a powerful magneto-electric machine, in producing a light of great steadiness and intensity between two points of gas coke: this light can be maintained without interruption so long as the magents are kept in rotation, and the charcoal continues unconsumed.

The machine consists of 48 pairs of permanent compound bar magnets, arranged in 6 parallel planes, so as to form a large compound wheel, between which the armatures, 160 in number, are arranged in 5 sets, the total amount of wire being about half a mile in length. The wires are insulated by cotton, and the contacts are so arranged as to maintain a continuous current in the same direction.

This is accomplished thus: One half of the helices are arranged so as to arrive on the poles of the magnet at the instant that the other half are exactly midway between the poles. Thus there are two distinct currents; and what may be called the dead point, that is, the point when the current becomes inverted in one series, occurs exactly at the time when the other current is at its maximum, so that if now the inverted currents can be again inverted in both of these distinct currents, and that the two now flowing in one direction can be united as one compound current, it is evident that the result will be a current nearly as constant as that from a galvanic battery, with the advantage of equable continuity. This is done by the two commutators, which consist each of two insulated rings of metal, of such a form at the periphery that two rollers or rubbers change sides from one disk to the other at the same instant that the current is reversed. Then, by combining the two commutators, a compound current is obtained that will produce a constant white light or any of the ordinary effects of the galvanic current. The quantity and the intensity of the induced current depend first, on the amount of magnetism induced in the soft iron; secondly, on the

facility with which the poles of the magnetized soft iron can be reversed; thirdly, on the velocity with which the change of polarity takes place; fourthly, on the length and diameter of the wire forming the helices.

The amount of magnetism induced in the soft iron depends on the size and strength of the steel magnets employed, and on the weight and softness of the iron in the helices; but in practice, the weight of the soft iron is limited by the weight of the steel magnets, for, if too heavy, the steel magnets will be slowly deprived of their magnetism.

The most advantageous proportion of iron in the armatures has been found by experiment to amount to $\frac{1}{50}$ of the weight of the steel magnets employed.

To facilitate the change of the poles, the soft iron cores of the helices are not solid pieces of iron, but are tubes, single, double, or treble, as it is found by experiment that the same weight of iron, when divided in this manner, loses or takes magnetism in much less time than when in a solid form.

There is a limit to the velocity to be employed when the maximum of electricity is required, for this reason. It has been already remarked that the amount of electricity depends on the amount of magnetism taken up, and that the soft iron takes time to become saturated, as it may be termed, with magnetism: hence, if the velocity with which the cores move from one pole of a magnet to another be too great, there will not be sufficient time for the cores to become saturated. But as again the quantity of electricity increases as the velocity increases, it is necessary to ascertain this maximum point exactly, which is easily done, either by experiment or calculation, based on certain data.

The steel bars weigh about 1 ton, and the wheel is made, by the aid of a small steam engine, to revolve with a rapidity varying from 150 to 250 times per minute. This light was for several months in successful operation at the South Foreland Lighthouse, and subsequently at Dungeness, the actual expense of fuel in working the engine being about equal to that of the oil formerly used, while the light is far more brilliant.

It was stated by Mr. Holmes, in a lecture given before the Society of Arts in December, 1863, from which the foregoing details are taken, that the light at Dungeness had then been in continuous use since the 6th June, 1862, and is equal photometrically to 14 of Fresnel's first-class lighthouse lamps. It is now again employed at the South Foreland.

Mr. Wilde (*Proc. Roy. Soc.* 1866, xv. 107 and *Phil. Trans.* 1867, 89) has lately contrived an apparatus by means of which, with very moderate magnetic power, he can, by employing sufficient mechanical power to produce rotation of his apparatus, obtain an extremely intense current of electricity.

The foundation of the arrangement is a magneto-electric machine of a peculiar form:—A compound hollow magnet cylinder, composed of two bars of soft iron connected by pieces of brass, was constructed with an internal diameter of 1·625 inches (4 centimetres). Upon this cylinder could be placed at pleasure 1 or more horse-shoe magnets. each weighing 1 lb., and capable of supporting a weight of about 10 lbs. These magnets were so arranged that all the poles of the same name rested upon the same soft iron bar of the magnet cylinder. In the interior of this cylinder a soft iron armature was made to revolve in close proximity to the internal surface, but without actually touching it. The cross section of this armature was somewhat like that of an ordinary railway rail, or like a capital H. Along the length of the armature, in the hollows thus formed, about 183 feet (56 metres) of insulated copper wire was coiled 0·03 inch

($0^{mm}.76$) in diameter, and the free ends of the wire were connected with a commutator fixed upon the axis of the armature, so as to receive the alternate currents in one direction only.*

A second machine, similar in construction to the first, but of larger dimensions, was then prepared, the magnet cylinder being 25 inches in length, and having a bore of 5 inches in diameter. In this second machine, instead of the permanent magnets, an electro-magnet, formed of two rectangular pieces of boiler plate, enveloped with coils of insulated copper wire, is employed. This electro-magnet is excited by the direct current of the magneto-electric machine, and the current excited in the armature of the electro-magnet is then transmitted through the coils which surround a second electro-magnet, and which is in this case of gigantic dimensions. The bore of the magnet cylinder of this machine is 10 inches in diameter, the electro-magnet weighs nearly 3 tons, and the weight of the entire machine is about $4\frac{1}{2}$ tons.

It is furnished with two different armatures, one for the production of currents of high tension, the other for producing large quantities of electricity. The armature for high tension is coiled with a bundle of 13 insulated copper wires, No. 11 gauge, or $\frac{1}{8}$ inch ($0^{min}.32$) in diameter, the coil is 376 feet (114 metres) in length, and weighs 232 lb. (105 kilogrammes). The armature for quantity is surrounded by layers of an insulated band of sheet copper, 67 feet long, weighing 344 lb., or nearly half as much more as the wire. The armature of each machine was driven with a uniform velocity of 1500 revolutions per minute. The stream of electricity obtained by means of this armature last described, when excited by sending the current from the small magneto-electric machine through the 5-inch electro-magnetic machine, by the current from which the large machine was constantly excited, surpassed the effects of any current ever before witnessed; a length of 15 inches of iron rod a quarter of an inch in thickness was melted by it, and a light between electrodes of gas coke half an inch square, was produced, "sufficient to cast the shadows of the flames of the street lamps a quarter of a mile distant upon the neighbouring walls."

Sir Charles Wheatstone and Mr. Ladd have constructed machines by which the small amount of residual magnetism exhibited by soft iron may be caused to produce powerful magneto-electric currents. If an armature covered with wire be caused to rotate at the end of a horse-shoe of soft iron, a feeble current of electricity is produced, and by causing a portion of this current to traverse a copper wire surrounding the soft iron, the magnetism of the latter is increased, and this again acts on the armature, producing more powerful currents, until the soft iron becomes a powerful electro-magnet, and the electric current very powerful. By this means it is seen that mechanical power is converted into electricity by the aid of the small amount of magnetism remaining in a piece of soft iron, or which is communicated to it by terrestrial induction.

Another machine of great power has recently been constructed by Gramme; since it differs considerably in construction from the instruments previously mentioned, it will require a more detailed description. If a ring of soft iron be placed between two opposite magnetic poles, it will become magnetized by induction, the part of the ring nearest to the north pole of the magnet will become south polar, and that opposite the south pole will be north polar. If the ring

---

* If the direct current of electricity thus obtained were transmitted through a galvanometer, it was found that the current produced, when the speed of rotation continued uniform, was very nearly in direct proportion to the number of magnets employed.

be supported on an axis at right angles to its plane, it may be caused to rotate between the poles by the application of a very moderate power, for during one complete revolution the edges of the ring will remain at a constant distance from the poles of the magnet; no energy is therefore required to overcome the magnetic attraction. During the rotation of the ring, the position of its poles will necessarily remain fixed with regard to the inducing magnet. A magnetized ring of this kind may be regarded as two semicircular magnets with their like poles in contact, and each with its neutral line half way between the extremities. If the neutral line of one side of the ring be surrounded by a loose loop of insulated wire, which can be moved round the ring from the neutral line, past one of the poles, to the other neutral line past the other pole, and back to its original position, electric currents will be induced in the wire, and it will be found on examination by a galvanometer, that in one complete rotation of the wire, two opposite currents will be induced, and that the reversal of the currents will take place during the passage of the loop across the neutral line. This follows necessarily from Faraday's original discovery of magneto-electric induction (311). Suppose a bar magnet placed with its north end upwards, the Ampèrian currents in this bar rotate in a direction opposite to the hands of a watch; if now a loop of wire be placed round the neutral line of the magnet, and then raised so as to slide it off the north end, a current will be induced in the wire in a direction contrary to watch-hands. If the loop be again placed on the magnet, the induced current will be in the same direction as the hands of a watch, so that on moving the loop from the neutral line off the pole the current is in one direction, and on returning it to its first position the current is in the opposite direction. Now, modify the experiment by removing the loop, turning it over and placing it on the pole so that the side of the wire that was at first upwards is now downwards, the current now induced, although reversed with regard to the magnet, flows in the same direction through the wire. Next take two bar magnets, place their north ends together, and move a loop of wire, connected as before with a galvanometer, from the neutral line of one magnet to the neutral line of the other: the action on the galvanometer in this case will be the same as in the previous one, the loop moving with the same side forwards off the first magnet and on to the second. Imagine each of the bar-magnets to be bent into a semicircle, and their similar poles placed in contact, we then have a magnetized ring, and when a loop of wire is carried from the neutral line on one side past the north poles to the neutral line on the other, a current will be induced in the wire in one direction, and when carried round the south poles to the other neutral line the current will be in the opposite direction. In Gramme's machine the ring is covered with a continuous insulated wire, and this annular bobbin and the soft-iron ring are attached to an axis, so that the whole can be rotated between the magnetic poles. It is evident that each turn of the coil will correspond to the loop in the experiment above described, so that in the half of the coil between the two neutral points on one side of the bobbin, the current will be flowing continuously in one direction, and in the other half it will be flowing in the opposite, the two positive currents meeting at one of the neutral lines, and the two negative currents at the other. In order to make use of these currents, a number of copper rods are connected at intervals with the continuous wire of the bobbin; these are kept insulated from one another, and project parallel to the axis of rotation of the bobbin. Against these rods two brushes of metallic wires are pressed, so that contact is made with two or three of the rods, whilst the corresponding portions of the bobbin are passing the neutral lines. In this machine no commutator is required, as the current is always in the same direction; it is also quite uniform in strength whatever may be the position of the coil. In the larger machines electro-magnets are used

for magnetizing the ring, a portion of the current, or an independent current from a separate coil, being employed.

(315 *a*) *Absolute Measures of Electro-Magnetic Quantities.*—Weber, in his "Electrical Measurements" (*Leipzig Transactions*), has introduced a method for the determination of all electrical quantities founded on purely mechanical considerations, and based on the metrical system; the metre, the gramme, and the second being the fundamental units.

The principal quantities to be measured are—

1. The quantity of electricity . . . . . Q
2. The strength of an electric current C
3. The electro-motive force which acts on the current . . E
4. The resistance of a conductor . . . . . R

If t is the time in seconds, then whatever be the system of measurement,

$$Q = Ct \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$E = CR. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Helmholtz and Thomson have shown, by the principle of conservation of energy, that if W is the work spent in causing the transfer of a quantity, Q, of electricity, by means of an electro-motive force, E,

$$W = QE \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation is analogous to the proposition in hydrostatics that the work done in forcing a volume V, of fluid, into a vessel under the pressure P, is equal to VP.

Weber defines a unit current of electricity as that which, if caused to traverse two circuits of unit area placed at a great distance from each other, would cause them to act on each other with the same force as two magnets of unit strength.

This gives a fourth datum, which, combined with equations (1) (2) (3), gives a complete system of electro-magnetic measures.

The most convenient practical method of measuring resistance is by comparison with a wire, the resistance of which has been determined by Weber's method. Weber obtained his unit of resistance by suddenly turning a coil of wire about a vertical axis, and measuring the quantity of electricity which was caused to traverse the coil by the inductive action of the earth's magnetism.

Thomson improved upon this method; and Jenkin, Clerk-Maxwell, and Balfour Stewart determined the resistance of a coil of wire revolving with known velocity, by means of its effect in altering the position of a small magnet suspended in the centre of the coil. For an account of these experiments, on which the British Association Unit of Resistance is founded (*note*, p. 550), see the Reports of the British Association for 1863, part I. 111, where an explanation of all the methods of electrical measurement is also given in an elementary form.

Weber has also employed a system founded on the phenomena of the stress between electrified bodies. We have then

$$\text{Repulsion} = \frac{Q\ Q'}{D^2}$$

where Q Q' are the quantities of electricity, and D the distance between them.

This system of measurement, which is called the Electro-static System, differs from the electro-dynamic system, and, according to Weber, the unit of electricity in the latter system (the metre, gramme, and second being the fundamental units), is 310,740,000 times that in the former.

From the known laws of electro-magnetic phenomena, combined with the

results of Weber, Clerk-Maxwell has calculated the rate at which an electro-magnetic disturbance of short duration would be propagated through air or vacuum. The result of this calculation shows that if light consists of a series of such electro-magnetic disturbances, it will be propagated with a velocity expressed by the same number as that which expresses the ratio of the two units of electricity. The actual velocity of light, as determined by various observers, has been stated at from 314 to 298 millions of metres per second. The number deduced from Weber's experiments is 310 millions.

§ VI. Thermo-Electricity.

(316) The phenomena due to the development of electricity by heat are arranged under the head of *thermo-electricity*,—a term which serves to recal to mind the manner in which the current originates in these cases. The present section contains a summary of the more important facts which have been ascertained on this subject.

As any obstruction to the passage of the electric current in a conductor occasions the development of heat, so any obstruction to the equal propagation of heat in a conducting circuit produces a current of electricity. This important result was first obtained by Seebeck, in the year 1822.

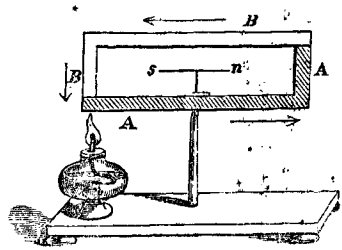
If the extremities of the wire of a sensitive galvanometer be united by means of a straight piece of platinum wire, this wire may be heated at any point at a distance from its connexions with the galvanometer wire, without producing a current through the circuit; but if the platinum wire be twisted into a loop, its molecular state at this point is slightly altered, and if heat be applied to the wire close to the loop and to the right of it, a current will flow through the apparatus from right to left, owing to the inequality of the conductivity, and the disturbance of regularity in the transmission of the current from the hotter to the colder portions. These effects are still more readily produced by dividing the wire into two portions, and coiling each extremity into a flat spiral. If one of these spirals be heated to redness, and be brought into contact with the cold spiral, deflection of the needle immediately follows, in a direction which indicates the flow of a current from the hotter to the colder portion. Metals such as bismuth or antimony, in which a crystalline structure is strongly developed, but which possess an inferior power of conducting electricity, display these thermo-electric phenomena in a more perfect degree. If one half of a ring or rectangular frame composed of either of these metals be heated, and the other half be kept cool, a current sufficient to deflect a magnetic needle suspended within the frame or ring, will be produced. Metals which are

better conductors, such as copper or silver, although they also show the phenomena, exhibit it much less distinctly.

Sir W. Thomson has found that if portions of a metallic wire be stretched by weights, and be connected with other portions of the same wire not so stretched, on applying heat to their junctions, a current is produced from the stretched to the unstretched wire through the heated point.

If the rectangle be composed of two dissimilar metals, as when a bar of antimony, A, A, fig. 262, is soldered to a bar of bismuth, B, B, the application of heat, such as the flame of a spirit lamp, to one of the junctions will cause deflection of the suspended needle, *n s*. A bar of bismuth when soldered to a copper wire, will readily deflect the needle of a galvanometer of moderate sensibility, if even the warmth of the hand only be applied to one of the junctions.

FIG. 262.



The earlier researches upon this subject appeared to show that so long as the resistances in the circuit continue unchanged, the current in circulation is exactly proportioned to the difference in temperature of the two junctions. Becquerel, relying upon the accuracy of this datum, has applied a thermo-electric pair of metals to the measurement of temperature. Amongst other experiments, he endeavoured to ascertain the temperature of flames. The metals which he employed were thin wires of platinum and palladium; the junction of the wires was introduced into different parts of the flame which, as might be supposed, were found to vary considerably in temperature. The proportionality of the current to the temperature, however, only holds good with those non-crystalline metals which do not oxidize when powerfully heated: and even these are liable to irregularity, so that the determination of temperatures by this means must not be relied on without special verifications, which, at high temperatures, can scarcely be effected with accuracy. For small differences of temperature, however, the thermo-electric pair or pile (317) surpasses in sensitiveness all other thermometric means at present in use.

If one of the junctions of a thermo-electric pair be maintained steadily at a low temperature, such as 0° C., whilst the temperature of the other junction is gradually raised, it happens with some combinations that the current increases in intensity up to a certain point, then declines, and is reversed; in the case of zinc and silver, the rise continues up to 248° (120° C.): then the current declines, becomes null, and ultimately is reversed, as the temperature con-

tinues to rise. Most probably this is due to the peculiar effect which heat has upon the crystalline structure of zinc. Iron and antimony exhibit the same effect, but to a less marked extent; and Thomson has extended the observation to a number of other metals. If gold, silver, copper, or brass be heated with iron, the direction of the current was observed by Cumming to be reversed at a red heat. So important is the influence of crystalline structure upon these results, that the thermo-electric power of bismuth is very materially reduced by the addition of a small percentage of tin, which impairs its tendency to crystallize.

An important connexion between the direction of the planes of cleavage and the direction of the thermo-electric current in crystalline metals was shown to exist by Svanberg. In bismuth and in antimony, for example, there is one particular plane of cleavage endowed with greater brilliancy than the rest. Bars of these metals, when placed with this plane of cleavage perpendicular to the direction of the current, are more highly negative than when placed in any other position; whilst, if a second plane of cleavage, somewhat less brilliant than the former, be placed across the line of current, the bar is more highly positive, thermo-electrically, than in any other position.

It may be stated that when two dissimilar metals are connected in any way so as to produce a closed circuit, an electric current is established each time that any difference in temperature is produced between the two points of contact; and the current is maintained so long as the difference of temperature continues.

The metals may be arranged in the following thermo-electric order:—

Bismuth	Copper and Silver
Mercury	Zinc
Lead	Iron
Tin	Antimony
Platinum	Tellurium.

When heated together, the current proceeds from those which stand first on the list towards those which follow them. It is to be remarked that the thermo-electric order of the metals is entirely different from the voltaic order. Matthiessen (*Phil. Trans.* 1858, 369) gives the following as the results of a careful series of experiments upon the thermo-electric order and energy of various bodies, for temperatures usually ranging between about 40° and 100° (4° and 38° C.). If the electro-motive force of the thermo-electric current excited between silver and copper be taken as

equal to 1 (the current passing from the copper to the silver at the heated junction), the strength of the current between silver and each metal in succession heated to the same point, will be represented by the numbers given in the following table. Where the negative sign is prefixed, the current is from the silver to the other metal at the heated junction; where the positive sign is prefixed, the current is from the other metal at the heated point towards the silver. The substances marked with an asterisk are supposed to have been chemically pure.

Thermo-Electric Order of Metals, &c.

	+		−
Bismuth, commercial, pressed wire	35·81	Gas coke, hard	0·057
*Bismuth, pressed wire ...	32·91	*Zinc, pressed wire	0·208
*Bismuth, cast	24·96	*Copper, voltaic	0·244
Crystallized bismuth, axial	24·59	*Cadmium	0·332
Crystal of bismuth, equatorial	17·17	Antimony, pressed wire ...	1·897
Cobalt	8·977	Strontium	2·028
Potassium	5·492	Lithium	3·768
Nickel	5·02	*Arsenic	3·828
Palladium	3·56	Calcium	4·260
Sodium	3·094	Iron, piano wire	5·218
*Mercury	2·524	Antimony, axial	6·965
Aluminium	1·283	Antimony, equatorial ...	9·435
Magnesium	1·175	*Red phosphorus	9·600
*Lead, pressed wire	1·029	*Antimony, cast...	9·871
*Tin, pressed wire	1·000	Alloy, 12 bismuth, 1 tin, cast	13·67
Copper wire	1·000	Alloy, 2 antimony, 1 zinc, cast	22·70
Platinum	0·723	*Tellurium	179·8
Iridium	0·163	*Selenium	290·0
*Antimony, pressed wire ...	0·036		
*Silver...	0·		

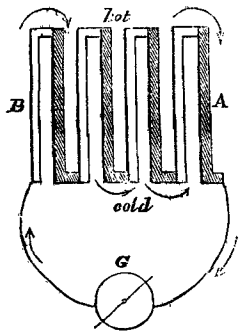
According to the experiments of Wheatstone and of Pouillet, who have arrived at the same result by very different methods, the electro-motive force of a pair of bismuth and copper, when one junction is maintained at 100° C. and the other at 0° C., is $\frac{1}{95}$ of that exerted between a pair of copper and zinc plates arranged in voltaic relation, as in Daniell's battery.

Thermo-electric circuits may also be formed with inferior conductors. Nobili brought the point of a heated cone of porcelain clay into contact with a cold cylinder of the same material, each connected with the galvanometer by cotton soaked in a conducting liquid: the current passed from the cone to the cylinder.

(317) *Thermo-Multiplier.*—By connecting together successive pairs of two different metals, and heating the alternate joints, whilst the other junctions are kept cool, a thermo-electric battery

may be constructed. The size of the elements which are employed contributes nothing to the effect, except in so far as by increasing the area of the conducting section, the conducting power of the circuit is increased. Such a battery will decompose a solution of potassic iodide, and Botto states that with a pile consisting of 100 pairs of platinum and iron wire, each $25^{mm.}$ long and $0.^{mm.}25$ in diameter, he succeeded in decomposing even dilute sulphuric acid. A thermo-electric current from a single pair is sufficient to convulse the limbs of a frog. The principle of the arrangement by which a *thermo-multiplier* or thermo-electric battery may be constructed is shown in fig. 263; to one series of junctions, a high temperature, to the other a low temperature may be applied; the shaded bars, A, represent bars of antimony, those in outline, B, indicate bars of bismuth. The intensity of such a current, however, is comparatively feeble, and the resistance which it experiences in traversing even metallic conductors of considerable diameter, such as the metallic bars themselves which are used in the construction of the battery, seriously reduces its power. A very cheap and effective thermo-electric pile may be made of wires of iron and German silver. Nobili and Melloni (*Ann. Chim. Phys.* 1831 [2], 198) applied a thermo-electric battery, consisting of 36 pairs of small bars of bismuth and antimony, to thermometric purposes. Such a battery was employed by Melloni, in his investigations on radiant heat, to the exclusion of almost every other thermoscopic means. When the alternate junctions of the bars at each end of the pile were covered with lamp-black, a coating was obtained which absorbed the radiations proceeding from a surface the temperature of which was much below that of the human body; even the amount of radiant heat emitted by insects could be estimated by connecting this battery with a galvanometer of extreme sensitiveness.*

Fig. 263.



The conductivity of red phosphorus and of selenium is so slight that neither of them can be used for the construction of

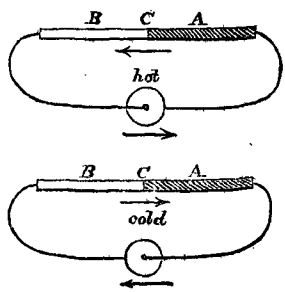
* Melloni used a galvanometer formed of copper wire $0.^{mm.}5$ in diameter, about 8 metres long, and arranged around the astatic needles in 40 convolutions. Much of the sensitiveness of the instrument depends upon the exact equality of the magnetization of the two needles: the compound needle should require from 55 to 60 seconds in order to complete an oscillation.

thermo-electric piles: that of tellurium is also small, but it is sufficient to admit of its use, and its electro-motive power, when opposed thermo-electrically to bismuth, is so great that a pile consisting of 8 pairs of these elements, where the alternate junctions are heated to 100° C., whilst the others are cooled to 0° C., will decompose a solution of cupric sulphate; and Matthiessen estimates the electro-motive force of 100 pairs of such a pile as equal to that of 4 cells of Daniell's arrangement. Bunsen has employed piles consisting of pyrolusite mixed with copper or platinum, or with copper pyrites combined with metallic copper, and with 10 pairs of such a thermopile he estimates that he has by a proper regulation of temperature an electro-motive force equal to 1 of Daniell's cells.

An effective form of thermopile was contrived by Marcus, who used for the positive element an alloy consisting of 10 parts of copper, 6 of zinc, and 6 of nickel; and for the negative element an alloy composed of 12 parts of antimony, 5 of zinc, and 1 of bismuth. If these alloys be cast into bars 7 inches long, half an inch broad, and an eighth of an inch thick, they may be screwed together in pairs, the alternate junctions being heated by a row of gas jets, whilst the other junctions are kept cool by immersion in a current of cold water: 60 pairs of such a battery were found by Wheatstone to have an electro-motive force equal to 2 of Daniell's cells; but Marcus states that with 6 pairs he has succeeded in decomposing water.

(318) In connexion with these thermo-electric effects, a curious observation was made by Peltier (*Ann. Chim. Phys.* 1834 [2], lvi. 379, and 1839, lxxi. 301):—When a weak current of electricity was transmitted through a compound bar of bismuth and antimony, from the antimony to the bismuth, as in No. 1, fig. 264, a thermometer, placed at the point of junction, was observed to rise several degrees, but when the current was reversed, as in No. 2, the temperature fell 4° C. In some later experiments, Peltier succeeded even in freezing water placed in a cavity drilled at the point of junction of the two metals, when the bar was cooled to 0° C. by immersion in snow (De La Rive, *Traité d'Electricité*, 1856, ii. 245). When feeble currents of equal intensity are transmitted through a compound metallic bar, whatever metals be employed, there is

FIG. 264.



a difference in the temperature at the points of junction, according to the direction in which the current is passing; the difference of temperature varying with the metals which are used. The fall of temperature occurs almost uniformly when the current passes through the two metals in the same direction as that in which the thermo-electric current would be produced by elevation of temperature.* For example, there is a rise of temperature when the current passes from iron to zinc, from iron to platinum, from iron to copper, from zinc to copper, from copper to bismuth, and from antimony to copper; but when the current is reversed between the same pairs, there is either a much smaller elevation, or in some cases even an actual depression of temperature. This subject has been discussed at great length by Clausius and by Thomson, in their researches on the mechanical theory of heat.

§ VII. Animal Electricity.

(319) Some fish, particularly the torpedo, the electrical eel (*Gymnotus electricus*), and the *Malapterurus electricus*, have the remarkable power of giving electrical shocks at pleasure, by means of an apparatus specially adapted to the purpose.

The torpedo, which is a species of ray, is a flat fish, tolerably abundant in the Mediterranean; it is provided with two electrical organs situated one on each side of the spine, near the head, occupying the whole thickness of the fish; these organs are supplied with large thick nerves, and it has been found that on cutting these nerves all voluntary electric power ceases: but according to Matteucci, the irritation of that end of the cut nerve which is attached to the organ in a lively torpedo, occasions the electric discharge, and even irritation of detached portions of the organ produces contraction in the limb of a frog recently killed, if the crural nerve of the frog be allowed to rest upon the organ of the torpedo. The structure of the electrical organs is gelatinous, and the material is divided by membranous septa into 400 or 500 columns, which have some resemblance to grains of rice in appearance; these columns run from the dorsal to the ventral surface of the fish, and are about the thickness of a goose-quill; the dorsal surface is positive, the ventral negative. The electricity is most strongly developed just at the points where the nerves enter the organ; a powerful shock is received on simultaneously touching the back and the belly of the fish at any part,

* An exception is presented in the case of lead and copper, and of tin and copper, in which the current is towards the copper from the heated metal.

but the shock obtained is strongest immediately over the two organs. A weaker shock is experienced on touching different parts even of the same surface, since the electric charge differs in intensity at different points of the same surface. Frequent discharges exhaust the animal quickly: the frequency of this discharge is under the control of the animal, but not its direction. The electric discharges of the torpedo are partly dissipated when the fish is immersed in water by the conducting power of this liquid, and Matteucci estimated that in air the shock given by the animal is four times as powerful as when it is in water.

(320) In the gymnotus, which is a fresh-water fish, tolerably abundant in the marshes of Surinam, and in the tributaries to the Orinoco, there are four electrical organs, a large and a small one on each side, running from the head to the tail of the animal. These organs, like those of the torpedo, are supplied with large nerves, and have a membranous structure, the septa running in a more or less longitudinal direction from the head towards the tail. The longer the column that produces the shock, the greater is the force of the electric discharge: the anterior portions of this animal are positive to the posterior, so that the strongest shocks are obtained by touching the fish simultaneously near the head and near the tail; but shocks more or less intense may be obtained from any part of the body, if the hands be separated for a short distance in the direction of the head and tail of the animal; scarcely any shock is felt if the hands be placed one on each side of the fish at the same distances from the head or the tail. So great is the electric energy of the animal, that the specimen which was exhibited in the Adelaide Gallery, 40 inches (about 1 metre) in length, was calculated by Faraday, at each medium discharge, to emit as great a force as the highest discharge of a Leyden battery of fifteen jars, exposing 3500 square inches (upwards of 2 square metres) of coated surface. Shocks differing in intensity with the position of the observer and his distance from the fish, were felt in all parts of the tub which contained it; this tub was 46 inches (1·16 metre) in diameter. The shocks from the gymnotus have power sufficient to kill or to stun fish; the same discharge produces a more powerful effect upon a large fish than it does upon a small one, since the larger animal exposes a larger conducting surface to the water through the mass of which the electricity is passing, and consequently it receives a more violent shock. On one occasion when a live fish was put into the tub, the animal was seen by Faraday to coil itself into the form of a semicircle, the fish lying across the diameter: this position was the one most favourable to

the full effect of the electrical discharge; an instant afterwards the fish floated motionless upon its side, deprived of life by the shock which it had received, and was then speedily devoured by the gymnotus.

The shock of both the torpedo and the gymnotus gives rise to momentary currents sufficient to deflect the galvanometer, to magnetize a needle, and to decompose potassic iodide: from both species, sparks have also been obtained between two insulated gold leaves properly connected with the fish.

(321) *The Muscular Current in Living Animals.*—The researches of Matteucci have shown that in the living animal an electrical current is perpetually circulating between the internal portion of a muscle and its external surface; this current is due probably to the chemical actions which are produced by the vital changes which are continually occurring in the organic tissue. The *muscular current*, as it has been termed, ceases to manifest itself in warm-blooded animals in a very few minutes after the life of the entire animal has terminated; but in cold-blooded animals, and especially in the frog, it continues for a much longer period. Vital contractility also continues in these animals for a longer period than in the higher orders of the vertebrata, and hence the frog has been extensively employed in researches of this description.

The following is one of the forms of experiment, devised by Matteucci, to show the existence of the muscular current:—Five or six frogs are killed by dividing the spinal column just below the head; the lower limbs are removed, and the integuments stripped off them; the thighs are next separated from the legs at the knee-joint, and are cut across transversely. The lower halves of these prepared thighs are then placed upon a varnished board, and so arranged that the knee-joint of one limb shall be in contact with the transverse section of the next, and thus a muscular pile is formed consisting of ten or twelve elements; the terminal pieces of this pile are each made to dip into a separate small cavity in the board, in which a little distilled water is placed. If the wires of a sensitive galvanometer be attached to a pair of platinum plates, and these plates be plunged simultaneously, one into each cavity in connexion with the muscular pile, a deviation of the galvanometer needle will be observed in a direction which indicates the existence of a current passing from the centre or cut transverse surface of the muscle towards its exterior.

Dubois Reymond, by the use of still more sensitive instruments, has shown that even the smallest shreds of muscular tissue

exhibit proof of the existence of such a current, and the conclusion which he draws from his experiments is the following:—Any point of the natural or artificial *longitudinal* section of a muscle is positive in relation to any point of the natural or artificial *transverse* section.

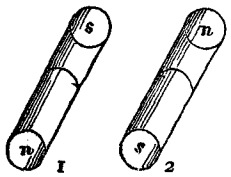
Interesting as this subject is in a chemical point of view, in connexion with the changes which take place in the circulating fluids, it would be irrelevant to our present purpose to pursue it further. The question belongs more properly to the physiologist than to the chemist; and the reader who desires fuller information upon this branch of inquiry is referred to the various papers of Matteucci, in the *Annales de Chimie*, and the *Philosophical Transactions*, and to the work of Dubois Reymond, or to the more recent systematic treatises on physiology.

§ VIII. Magnetic Polarization of Light—Diamagnetism.

(322) *Influence of Magnetism on Polarized Light transmitted through Uncrystallized Transparent Bodies.*—Allusion has been already made (127) to a peculiar kind of polarization to which light is subject, when transmitted through certain transparent media, which are under the influence of magnets of high power. Some transparent bodies are better fitted than others to exhibit this phenomenon. Some years ago Faraday (*Phil. Trans.* 1830, 1) prepared a peculiar kind of glass for optical purposes; it consisted of a mixture of silicate and borate of lead, and was much denser than ordinary flint glass: this glass is particularly well adapted to display the effects of magnetic polarization (*Phil. Trans.* 1846, 1). Let a piece of this glass which has been properly annealed be cut into the form of a rectangular bar or prism, terminated by flat parallel faces, and let it be placed between the poles of a powerful electro-magnet not in action, the axis of the prism being parallel to a line which joins the two poles—in fact in the direction of the keeper of a horse-shoe magnet. A ray of polarized light may be transmitted along the axis of the glass bar, and if examined by an analysing plate in the usual manner (120) the light will disappear when the plane of reflection from the analysing plate is at right angles to the plane of polarization. If, now, whilst the polarized ray is at the point of maximum obscuration, the soft iron be magnetized by the action of the battery, the light will instantly reappear, and if white light be used, the reflected ray will be coloured. The moment that the connexion with the battery is broken, the light will disappear; but it will

again become visible each time that the iron is rendered magnetic. If the north end of the magnet be towards the observer, the rotation of the plane of polarization is to the right, as represented in fig. 265, No. 1; but if the direction of the magnetism be reversed, so that the south end is nearest the observer, the rotation is to the left, as in No. 2.

FIG. 265.



Different bodies, when placed between the poles of an electro-magnet, possess the property of causing the ray to rotate in different degrees, but all singly refracting solids and liquids manifest it: in magnetized gases, and *in vacuo*, no such effects have been discovered. The extent of the rotation is, *cæteris paribus*, directly as the intensity of the magnetism, and as the length of the medium traversed by the ray. By placing the transparent bodies in the axis of a coil of wire conveying an electric current, the same effects are produced, but in a lower degree: the more numerous the coils of the helix, and the longer the column of the transparent body which is traversed by the ray, the greater is the extent of the rotation. If while a ray of polarized light is traversing a diamagnetic medium (324) an electric current be passed round the ray, in a plane perpendicular to the direction of the ray, the rotation occurs in the same direction as that in which the current is passing. The interposition of bodies which are not susceptible of magnetism, between the coils of the helix and the transparent body placed in its axis, does not sensibly affect the polarizing action, but the interposition of a hollow iron core between the helix and the transparent body in its axis, in some cases greatly heightens the effect, in others it neutralizes it, the rotatory influence varying with the thickness of the core.

Matteucci found that by elevating the temperature of a bar of heavy glass to about 600° (316° C.), the rotatory power is increased by about one-third, when compared with the effect of the same bar at ordinary temperatures. According to Matthiessen, fused phosphoric acid, agate, fluor spar, and flint, exhibit no susceptibility to magnetic polarization. Bertin (*Ann. Chim. Phys.* 1848 [3], xxiii. 31) gives the following rotatory power for columns of equal length of various bodies at ordinary temperatures, assuming that of heavy glass as equal to 1:—

Heavy glass	1·00
Stannic chloride	0·77
Carbonic disulphide	0·74

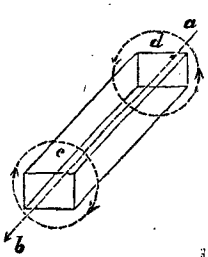
Common flint glass	0·53
Phosphorous chloride (PCl_3) . . .	0·51
Water	0·25
Alcohol (density 0·850)	0·18
Ether	0·15

The salts of calcium, of zinc, and of magnesium, as well as many other saline substances, increase the rotatory power of water, when added to it, the effect being proportioned to the strength of the solution. Verdet has determined by careful measurement (*Ann. Chim. Phys.* 1853 [3], lii. 129) the extent to which this rotatory power is possessed by various bodies in solution; and the same observer has shown that many magnetic bodies experience a rotation in a direction the reverse of that produced in diamagnetic bodies; for example, the addition of a salt of iron to water diminishes the rotatory power of the liquid; an aqueous solution of ferric chloride, containing 40 per cent. of the salt, gives a *negative* rotation, which is five or six times as powerful as the positive rotation possessed by water. Salts of chromium, titanium, cerium, uranium, and lanthanum produce a similar effect; whilst the salts of nickel and cobalt, which are also magnetic, produce a *positive* effect, and increase the ordinary rotatory power. Potassic ferrocyanide, although it contains iron, exerts a positive rotatory effect.

Bodies, such as oil of turpentin, which naturally produce coloured rotatory polarization (126) have the power exalted, annihilated, or reversed, according to the direction and intensity of the electric current which is transmitted through the coil. The polarization produced by magnetism differs from the ordinary coloured rotatory polarization shown by oil of turpentin, in this remarkable particular—viz., that the magnetic rotation is always in the same direction as that of the current which circulates around the coil.

Let *c d*, fig. 266, represent a vessel filled with oil of turpentin endowed with right-handed rotation, and let *a b* be a polarized ray. If the ray proceed from *a* to the observer at *b*, the rotation will of course appear to be right-handed to him, as shown by the circle, *c*; and if from *b* to *a*, the rotation will still appear to be right-handed to the observer at *a*, as shown by the circle, *d*. If now a current be passed round *c d*, in the direction of the circular arrow at *c*, the rotation to the observer at *b*

FIG. 266.



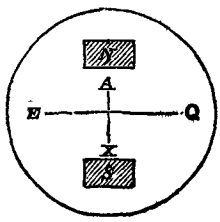
will appear to be increased; while to an observer at *a*, it will appear to be neutralized or reversed.

These effects upon the polarized ray are due to the temporary strain of the molecules of the transparent bodies while under the influence of the magnet. Matteucci found that by submitting the glass or other transparent body to compression, he could modify or diminish the extent of the rotation which the same substance would produce when submitted to equal electro-magnetic force, in circumstances in other respects similar.

(323) *Magnetism of Bodies in general.*—It was formerly imagined since iron was susceptible of magnetism in a high degree, nickel in an inferior degree, and cobalt in a degree still less, that all other substances might also be magnetic, although to an extent so minute as to elude the ordinary means of observation. Moreover, as experiment has proved that a reduction of temperature exalts the magnetic power of iron and of nickel, it seemed not unreasonable to anticipate that by extreme depression of temperature a point might be attained at which every species of matter would show itself obedient to the magnet. Experiments made upon this subject at very low temperatures have not, however, justified these expectations. The employment of magnets of unusual power has, on the other hand, revealed the existence of a susceptibility to magnetism in cases where under ordinary circumstances it had not been observed. (Faraday, *Phil. Trans.* 1846, 21.)

Before adverting to these experiments, it will be advisable to define clearly the different parts of the space between the two poles where the magnetic action is manifested. Let us suppose that we are looking down upon the poles N S (fig. 267), of a powerful horse-shoe magnet; the space between them has been termed by Faraday *the magnetic field;* the line A, X, will give the direction of its *axis;* the line E, Q, which is in the same horizontal plane, but at right angles to A, X, will form the *equator* of the magnetic field.

FIG. 267.

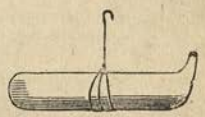


A bar of iron suspended by its centre above such a magnet, will take a horizontal direction parallel to the axis, A, X, and is said to point *axially*. By using electro-magnets of enormous power (303) many bodies not usually reputed to be magnetic will take the axial position like a bar of iron. For example, if an elongated fragment of hæmatite, or native ferric oxide, which is indifferent to a common magnet, be suspended horizontally at its centre by a few fibres of silk between the poles of such an electro-

magnet, it will point axially; even a sheet of writing-paper rolled up so as to form a short cylinder will, usually, owing to the small quantity of iron or of cobalt that it contains, assume a similar direction.

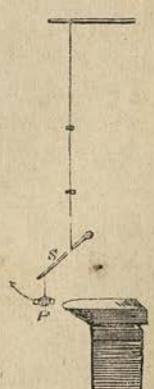
Faraday has found as a general rule that the salts of the magnetic metals are themselves magnetic, provided that these metals enter into the *basyl* of the salts. For instance, crystals of ferrous sulphate placed in a thin glass tube, which is not magnetic, will cause the tube to point axially. Such salts preserve their magnetic properties even when dissolved in water: if the solution be placed in a glass tube of the form shown in fig. 268, the tube, when suspended by a loop of copper wire and a few fibres of raw silk, will take an axial position between the poles of the magnet. Solutions of nickelous and cobaltous sulphate act in a manner similar to the solutions of the salts of iron. The pure salts of chromium and of manganese have in like manner proved to be magnetic, and hence these metals themselves are inferred to be so, although, from the high temperature required to reduce them to the metallic condition, it is difficult to obtain the metals in mass in such a state of chemical purity as would enable the fact to be verified by experiments upon the metals themselves.

FIG. 268.



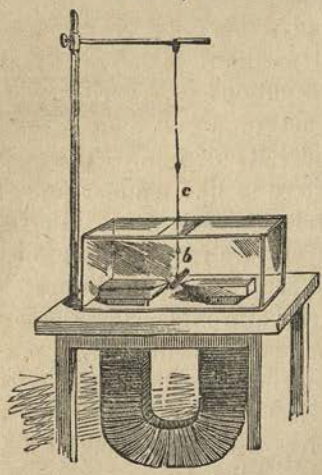
(324) *Diamagnetism.*—All the magnetic bodies mentioned above are attracted indifferently by either magnetic pole; and, if of elongated form, they place themselves with their longest diameter in the axial direction when suspended by their centre between two contrary magnetic poles. It is, however, far from being true that all substances are magnetic. Bodies exist which, when brought near to a magnetic pole, are repelled instead of being attracted: such substances have been termed *diamagnetic*. If a straw (s, fig. 269) be suspended horizontally by a silk fibre, and from one extremity of the straw a small piece of phosphorus, P, be supported in a ring of fine copper wire, repulsion of the phosphorus will be produced indifferently by either pole. In such an experiment it will be found convenient to place a soft iron armature, bevelled off to a blunt point, upon the pole of the magnet, in order to concentrate the power, because the repulsion is very feeble when compared with the attraction developed in iron. If a stick of phosphorus be suspended between

FIG. 269.



the two poles of the electro-magnet, it takes the *equatorial* position, assuming a direction at right angles to that of a bar of iron, the phosphorus being repelled by each pole to the greatest distance possible. Phosphorus, it will be observed, is a non-conductor of electricity; but some of the metals, of which bismuth and antimony are the most remarkable, exhibit this repulsion in a still higher degree. Substances of an organic nature, such as slices of wood, apple, potato, or flesh, likewise show this diamagnetic power, though not strongly. In fact, all bodies which are not magnetic, exhibit diamagnetic properties.

FIG. 270.



Owing to the feeble amount of these repulsions, it is necessary to screen the objects under experiment from the influence of currents of air, by surrounding them with a glass-case, as represented in fig. 270, in which *b* represents a bar of bismuth, or other diamagnetic body, delicately suspended by a few fibres of unspun silk, *c*. The bismuth bar is shown in the equatorial position between the two poles of the electro-magnet which project through apertures made for their reception in the table.

(325) *Diamagnetism of Gases.*—The earlier experiments upon the gases, owing to the very small amount of ponderable matter to be acted upon, gave results which seemed to prove that they were indifferent to the influence of the magnet; but subsequent researches have shown that even the different gases and vapours are susceptible of the diamagnetic influence in a degree which varies with the nature of the gas.—(Faraday, *Phil. Mag.* 1847 [3], xxxi. 401.)

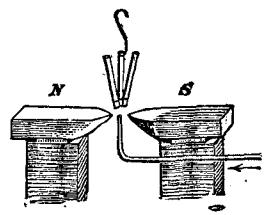
The gases upon which experiments were made by Faraday appear to stand in the following order, beginning with those which are least diamagnetic:—atmospheric air, nitric oxide, nitrogen, carbonic anhydride, nitrous oxide, carbonic oxide, hydrogen, coal gas, olefiant gas, hydrochloric acid, ammonia and chlorine.

Elevation of temperature exalts the diamagnetism,—a stream of hot oxygen appearing to be diamagnetic in an atmosphere of cold oxygen. A similar result was obtained with all such gases as were compared with each other at high and at low tem-

peratures. On the other hand, depression of temperature lowers the diamagnetism, so that a current of cooled gas when allowed to flow into a warmer atmosphere of the same kind, takes an axial position in the magnetic field. If a stream of one gas be allowed to escape into an atmosphere of a second gas more diamagnetic than itself, the less diamagnetic gas takes the axial position; when atmospheric air, for instance, is made to flow into coal gas, the air takes the axial or magnetic position between the poles: though air itself would take the equatorial position in oxygen gas. The diamagnetism of gases was first indicated in an experiment by Bancalari: he found that the flame of burning bodies was influenced by the action of a powerful electro-magnet. This effect is beautifully exhibited by simply placing the flame of a taper, or of any combustible substance, between the poles of the magnet, when in action; the flame appears to be repelled towards either side by the poles, and if the magnet be sufficiently powerful, the flame divides into two streams, which pass off horizontally, one on either side, in the equatorial direction. If the taper be extinguished, whilst the wick still continues to glow, the ascending column of smoke when placed between the poles of the magnet exhibits these motions equally well.

The following simple contrivance was employed by Faraday to show the position assumed by the different gases. A bent tube conveyed the gas for experiment in a very slow but continuous stream into the centre of the magnetic field; generally a piece of paper, moistened with a solution of ammonia, was placed in the bent tube. Supposing the gas to be lighter than air, three wide glass tubes, open at each end, and three or four inches (8 or 10 centimetres) long, were suspended with their lower apertures in the equatorial line, as represented in fig. 271, with the middle tube just above the bent tube for the delivery of the gas. In each tube a piece of paper moistened with hydrochloric acid was suspended. The whole was screened from currents of air by plates of glass. So long as the iron was not magnetized, the gas flowed readily up the axis of the middle tube; but on bringing the electro-magnet into action, the gas, instead of passing directly up the central tube, was, when more diamagnetic than air, diverted into each of the side tubes; and the currents were rendered visible by the white fumes produced when the ammonia carried by the gas came into contact

FIG. 271.



with the vapours of the acid contained in the tube. If the gas under experiment were heavier than atmospheric air, the position of all the tubes was inverted, and in place of ascending currents, descending currents were obtained. The action of the magnet upon the different gases was also shown by blowing soap bubbles, filled with each gas for trial, upon the end of a capillary tube, and bringing the suspended bubble near to the pole of the magnet; on completing the circuit the bubble was attracted or repelled according as the gas was magnetic or diamagnetic.

By suspending a feebly magnetic glass tube, attached to the thread of a delicate torsion balance, between the magnetic poles successively in oxygen and *in vacuo*, E. Becquerel (*Ann. Chim. Phys.* 1850 [3], xxviii. 324) found that the tube was less strongly attracted in oxygen than in the exhausted receiver, and by varying the experiment in different ways he succeeded in proving that oxygen is a decidedly magnetic body; he has calculated that a cubic metre of oxygen, which at 0° C. and $760^{mm.}$ Bar. weighs 1·4298 kilo., if it were condensed till it had a specific gravity equal to that of iron, would act upon a magnetic needle with a force equal to that of a little cube of iron weighing $540^{mgrms.}$: or that the magnetism of oxygen is to that of metallic iron as 1 : 2647. He computes that the magnetic effect of the oxygen in the air is equal to that of a shell of metallic iron $\frac{1}{250}$ of an inch ($0^{mm.}1$) in thickness surrounding the globe of the earth.

The fact of the magnetism of oxygen was first suggested by Faraday (*Phil. Mag.* 1847 [3], xxxi. 412) and was amply proved by him (*Phil. Trans.* 1851, 23), independently of Becquerel. He has further ascertained that, like iron, it loses its magnetism when strongly heated, but recovers it when the temperature falls. In this diminution in magnetic intensity as the temperature rises, he considers, probably lies the explanation of the diurnal variations of the needle, the cause of which has so much perplexed magnetic observers: the explanation is, however, not regarded as adequate by some eminent magneticians.

(326) The following table contains a list of various substances arranged in the order of their magnetic* and diamagnetic powers, as approximately determined by Faraday:—

* Faraday regards all substances as magnetic, and designates those substances generally termed magnetic, as *para*magnetic, in contradistinction to those which are diamagnetic.

Magnetic.	*Diamagnetic.*
Iron	Bismuth
Nickel	Phosphorus
Cobalt	Antimony
Manganese	Zinc
Chromium	Silico-borate of lead
Cerium	Tin
Titanium	Cadmium
Palladium	Sodium
Crown glass	Flint glass
Platinum	Mercury
Osmium	Lead
Oxygen	Silver
	Copper
	Water
	Gold
	Alcohol
	Ether
	Arsenic
	Uranium
	Rhodium
	Iridium
	Tungsten
Nitrogen.	

It is worthy of particular remark that the same substance may appear to be either magnetic or diamagnetic according to the nature of the medium in which it is placed. If a glass rod be suspended horizontally in a vessel of water, which is a strongly diamagnetic body, it will point axially, like a rod of iron: whereas the same rod, if suspended in a solution of ferrous sulphate, which is magnetic, will point in the equatorial direction. In like manner a tube containing a solution of ferrous sulphate will in pure water seem to be magnetic, while in a still stronger solution of the sulphate it will act as a diamagnetic substance; just as a soap bubble filled with carbonic anhydride, which is heavier than air, will fall to the ground, while if filled with hydrogen, which is much lighter than the atmosphere, it will ascend.

Air, in consequence of its containing oxygen in an uncombined condition, is a magnetic substance.

(327) *The same Elements in combination may be Magnetic or Diamagnetic according to the nature of the Compound.*—One of the most interesting peculiarities of diamagnetism is exhibited in

the circumstance that the same body may assume the magnetic or the diamagnetic state according to the nature of the compound which it forms. A metal may, for example, occur as the basic or electro-positive constituent of a compound, or it may enter into the composition of those substances which form the acid or electro-negative constituent of the compound. A good illustration of the difference thus produced occurs in the case of iron. Iron acts as a basyl in the crystals of green vitriol ($FeSO_4$, 7 H_2O), of which the metal forms about a fifth by weight, and it gives them a decidedly magnetic power; but in potassic ferrocyanide (K_4FeCy_6, 3 H_2O), which also contains iron, to the extent of more than an eighth of its weight, the crystals are diamagnetic. The iron in this case occurs in the electro-negative constituent of the salt, and not as a basyl.* In the same way, potassic dichromate (K_2CrO_4, CrO_3), where the chromium forms part of the acid radicle, is diamagnetic, whilst chromic sulphate (Cr_2 3 SO_4), where the metal acts as a basyl, is decidedly magnetic. Some of the compounds of cobalt exhibit analogous differences.

(328) *Influence of Structure on Diamagnetism.*—In prosecuting this subject, Tyndall and Knoblauch (*Phil. Mag.* 1850 [3], xxxvi. 178, and xxxvii. 1) have been led to the conclusion that a substance may appear to be either magnetic or diamagnetic according to the arrangement of its component particles. It must not, however, be supposed that there is not a real distinction between the two classes of substances; but that, under certain circumstances, a truly magnetic body may appear to be diamagnetic, and a body truly diamagnetic may appear to be magnetic. The following experiment may be cited in order to explain this point. A small flat circular disk was prepared with a paste of wheaten flour; and in this disk a number of short pieces of iron wire were placed, all parallel to each other and all passing from one surface of the disk to the other, perpendicularly to its two faces. This disk was suspended from a fibre of silk, by its edge, in a vertical direction, between the poles of an electro-magnet; but although it was undoubtedly magnetic, the plate placed itself with its faces parallel to the equator of the magnetic field. Each of the short pieces of wire, however, had assumed the axial position, although the disk as a whole arranged itself in a diamagnetic position.

When a similar disk was prepared in which threads of bismuth

* It is, however, remarkable that the red prussiate, or potassic ferricyanide ($K_6Fe_2Cy_{12}$), is, according to Plucker's observation, distinctly, though feebly magnetic. Faraday enumerates it among the diamagnetic class.

were substituted for the iron wire, the disk placed itself in the magnetic direction, with its faces parallel to the axis of the magnetic field. The bismuth, however, is unquestionably diamagnetic, and each of the pieces of this metal which the plate contained assumed the diamagnetic direction.

The conclusion which Tyndall and Knoblauch draw from these experiments is, that if, in a magnetic or in a diamagnetic mass, there be one particular direction in which the particles which compose it are more closely approximated to each other than in any other direction, the line which corresponds to this direction of greatest density will be the one in which the magnetic or diamagnetic action is most strongly marked. One of the experiments made in support of this view is the following:—Powdered bismuth was formed by means of gum-water into a mass sufficiently coherent to be worked into a small cylindrical bar about an inch ($25^{mm.}$) long and a quarter of an inch ($6^{mm.}$) thick. When this cylinder was suspended by its centre, in a horizontal direction between the poles of the electro-magnet, it pointed equatorially as an ordinary bar of bismuth would have done; but when the same cylinder was compressed laterally, so as to form a flat plate, it assumed a direction with its faces parallel to the axial position, although its length in some cases was ten times as great as its thickness.

Again, ferrous carbonate is a magnetic body: if reduced to fine powder, and formed into a cylinder similar to that made with the bismuth, it will point axially, or like a magnet, between the poles; but if compressed into a plate, this plate will set with its faces parallel to the equatorial direction. Here, in each case, those parts in which the particles of the bismuth, or the salt of iron, are by compression brought the nearest to each other, are those in which the diamagnetic or the magnetic action predominates. It is by an application of this principle that Tyndall and Knoblauch account for the fact discovered by Plucker (*Pogg. Ann.* 1847, lxxii. 315), that in all crystalline bodies belonging to those systems which exercise a doubly refractive influence on light, the optic axis assumes a definite direction under the influence of the electro-magnet. Assuming that the optic axis of a crystal is the direction in which the particles of the crystal have experienced the greatest degree of condensation, the effects obtained by experiment admit of explanation. The position assumed by the optic axis is not uniformly the same in different specimens of the same substance, although in the same specimen it is always the same. For example: Iceland spar, when pure, is a diamag-

netic substance, but, if it contains ferrous carbonate, it exhibits magnetic properties. In the course of their researches Tyndall and Knoblauch took pieces from several specimens of Iceland spar, some of which were magnetic, others diamagnetic. These different samples were cut into the form of disks, or flat circular plates, the surfaces of which were parallel to the optic axis of the crystals. When the disks were suspended horizontally at their centres between the poles of an electro-magnet, so that the optic axis of the crystal was in a horizontal plane, each disk always assumed a determinate direction. When the disk was taken from a magnetic crystal, the optic axis placed itself axially between the poles; when from a diamagnetic crystal, the optic axis assumed the equatorial direction. Thus it appears, that whether the crystal be magnetic or diamagnetic, the action is exhibited in each case most powerfully in the direction of the optic axis, which is assumed to be the line in which the particles are most closely approximated to each other. Faraday has shown that the directive force of the crystal, whether magnetic or diamagnetic, diminishes as the temperature rises.

(329) *Law of Diamagnetic Repulsion.*—It has been ascertained by E. Becquerel and by Tyndall that the diamagnetic repulsion, as measured by means of the torsion balance, is as the square of the intensity of the current. The phenomena of diamagnetism may be accounted for, as was remarked by Faraday, on the supposition that electric currents are circulating around the particles of the diamagnetic body in a direction the reverse of those which are supposed to exist in magnetic bodies, though he was unable to satisfy himself, by experiment, of the existence of such polarity; but the experiments of Reich, of Weber, and of Tyndall (*Phil. Trans.* 1855, 1, and 1856, 237), appear to have proved conclusively that bodies which are under diamagnetic influence, exhibit polar characters. The polarity of these bodies is such that a diamagnetic substance possesses a feeble magnetic polarity, the magnetism of each pole being *similar* to that of the pole of the inducing magnet in its vicinity; whereas in an ordinary magnetic substance the inducing magnetism is *opposite* to that of the magnetic pole by which the magnetism is elicited.

The principle of Weber's beautiful apparatus, with which Tyndall's decisive experiments were made, will be understood without difficulty. Let H, H′ (fig. 272) represent two similar vertical helices of copper wire; *a b*, *c d*, two bars of bismuth or other diamagnetic body attached to cords, which pass over the wheels, w, w′, so that they can, by moving one of the wheels, be placed, at pleasure, in either of the positions shown in fig. 274, 1 and 2. *n s* represents one of a pair of bar magnets, arranged astatically, and delicately suspended side

by side by a few fibres of unspun silk, T. M is a mirror attached to the centre of the magnet, and by viewing a scale reflected in this mirror through a telescope at a distance of 3 or 4 metres, the smallest deflection of the magnets may be estimated and measured. On transmitting a voltaic current from one or two of Grove's cells through the coils in opposite directions, the bismuth bars within the helices will become diamagnetized; and by carefully raising or lowering the astatic bars, *n s*, *s n*, shown in section with the coils H, H′ in fig. 273, until they

FIG. 272.

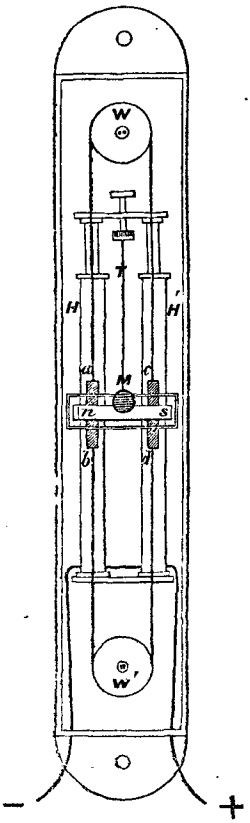


FIG. 273.

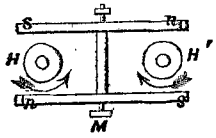
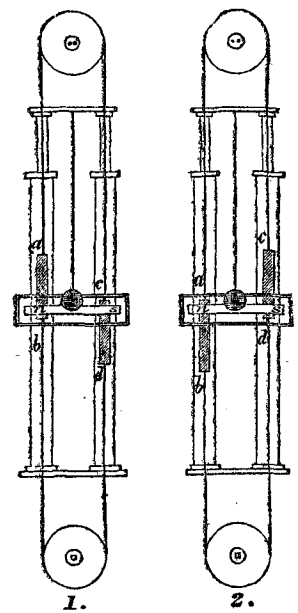


FIG. 274.



are opposite the middle of the coils, a position may be found in which the magnets become indifferent to the action of the current. If, whilst the apparatus is thus arranged, the wheel w be turned to the right, the bismuth bars will be brought into the position fig. 274, 1, and a deflection of the astatic magnets will be effected. The lower end, *b*, of one bismuth bar, if polar, would be (from the reversed direction of the currents in the helices) in the same condition as the upper end, *c*, of the other bismuth bar, and each will therefore attract one particular end, say the north, of each magnet composing the astatic combination, and would repel the south end; each conspiring to produce a deflection of both magnets in the same direction: but on turning the wheel to the left, so as to bring the bismuth bars into the position shown in 274, 2, the astatic combination will be deflected to an equal extent in the opposite direction.

These effects are most marked with bodies like bismuth and antimony, which have the greatest diamagnetic energy; but they are also distinctly shown even in non-conducting bodies, such as heavy glass, phosphorus, and sulphur.

If solid bismuth give a deviation which is represented by 75 divisions of the scale employed, the following table will represent the action, found by Tyndall, of the other bodies enumerated in it:—

Bismuth	75	Heavy glass	4
Powdered bismuth	37	Phosphorus	4
Antimony	13·5	Distilled water	4
Carbonic disulphide	5·5	Calc-spar	2
White marble	5	Nitre	1·7

(330) *Energy; Conservation of Energy; Mutual Relations of Different Kinds of Energy.*—The progress of scientific inquiries for many years past has been of such a nature as to produce a growing conviction in the minds of the active cultivators of science, that energy is equally indestructible with matter; and that, consequently, the amount of energy which is in operation in the earth (probably in the solar system), is as definite as that of the material elements through which its existence is made known to us.

That the quantity of *energy* associated with matter is definite, may be illustrated in various ways; one or two examples must suffice. The first which we will select will show the fixity in the proportion of heat which is associated with a given quantity of matter. A kilogramme of charcoal when burned with a free supply of air, combines with $2\frac{2}{3}$ kilos. of oxygen, and produces $3\frac{2}{3}$ kilos. of carbonic anhydride. The chemical action produced by this combustion is attended with the evolution of a definite quantity of heat: and this amount of heat, if it be applied without loss, is sufficient to convert 13·01 kilos. of water at 15° C., into steam at 100° C.: associated with each kilogramme of charcoal there must therefore be a definite amount of energy which is brought into action when that charcoal is burned. A different but equally definite amount of heat is emitted when a kilo. of phosphorus, of sulphur, of hydrogen, or of any other combustible is burned with free access of air (199 *et seq.*). The quantity of electricity associated with a given quantity of matter is equally definite (282). When a piece of amalgamated zinc is placed in voltaic relation with a plate of platinum in dilute sulphuric acid, for each kilo. of zinc which is dissolved, a quantity of electricity is liberated, by means of which a kilo. of metallic copper may be separated from the solution of a sufficient quantity of cupric sulphate, or $3\frac{1}{5}$ kilos. of silver may be reduced from a solution of argentic nitrate.

But it appears further, that there is no such thing as a destruction of energy. The cases in which a superficial examination would lead to the conclusion that energy is annihilated, show on closer investigation that such a supposition is erroneous.*

It will be found that in all cases in which energy disappears, it has expended itself either in eliciting or setting into action an equivalent amount of some other kind of energy, or else it has temporarily disappeared in producing a definite amount of motion. In this case it is especially to be remarked that the amount of motion which it has thus brought into action, when that motion is destroyed, will again give rise either to an equal amount of the energy which originally produced it, or to an equivalent quantity of some other manifestation of energy.

For example, the chemical action between charcoal and oxygen terminates as soon as the charcoal is wholly converted into carbonic anhydride; and a quantity of heat, which is equivalent to that amount of chemical action, remains as the representative of the force thus expended. The heat which has thus been developed is ready to do other work; it may be employed in converting a certain quantity of water into steam, and the steam so obtained can be applied to the production of motion, the amount of which may be measured by determining the number of kilos. which can be lifted through a given height by the steam thus produced. Motion may again be made to produce heat, and, as Joule's experiments show, the quantity of heat thus rendered manifest is strictly determined by the amount of motion which is applied to its development.

It appears, however, not only that energy is definite in its amount, and indestructible, but that many of the more important varieties of energy are intimately related, and are capable in turn of eliciting each other. The actions amongst which such mutual relations have been experimentally proved to exist in the closest manner, are those of light, heat, electricity, magnetism, and chemical attraction. The transfer of any one of these manifestations from one point to another, or, in other words, the exertion of any one of these actions is always attended with a collateral manifestation of one or more of the other forms. In the action of a voltaic circuit, consisting of a single pair of plates of zinc and platinum, the solution of a certain quantity

* Even in the case of light, for which, when it has disappeared by absorption, no quantitative measurement free from doubt has yet been given, it is probable that conversion into heat takes place.

of zinc, *chemical action* between the zinc and the acid, may be made to develope several actions—viz.: 1. *Electricity*, but there is no direct manifestation of this action so long as the circuit is closed. 2. *Chemical action:* if a voltameter, charged with a solution of cupric sulphate, be interposed in the circuit between two electrodes of copper, a certain quantity of copper, corresponding to the zinc which is being dissolved in the battery, will be deposited on one electrode, whilst a corresponding amount of copper will be dissolved from the other electrode. Here is a chemical action, which corresponds in amount to that which is taking place between the zinc and sulphuric acid in the active cell of the battery. 3. *Magnetism:* if the connecting wire be coiled round a piece of soft iron, the iron will become powerfully magnetic for the time during which the current is traversing the conducting wire. 4. *Heat:* if, whilst the voltameter, the electro-magnet, and the galvanometer are still included in the circuit, part of the circuit be composed of a thin wire which traverses the bulb of Harris's air thermometer, an elevation of temperature in the wire proportioned to the amount of electricity in circulation will be obtained, but in proportion to the quantity of heat evolved, the chemical action is lessened, and the strength of the magnet is reduced; and 5. *Light:* on interrupting the connexion of any part of the circuit a bright spark is obtained. Chemical attraction, then, whilst in operation, can throw a current of electricity into circulation, and a current of electricity will develope an equivalent amount of magnetism in a direction at right angles to such current. It also produces in conductors, heat proportioned to the resistance which it experiences, and if the heat be sufficiently intense, it is attended with the emission of light.

The observations of Favre already quoted (280) showing the dependence of the quantity of heat evolved in any given circuit upon the amount of magnetic or mechanical work which it is producing, afford interesting additional proofs of the important proposition that energy is never really either generated or destroyed; it may, however, be dissipated, so as to become unavailable. Man has but the power to elicit it when latent, to transfer the energy to new points, or to change the form of its manifestation so as to obtain an equivalent amount of work under new conditions, but when mechanical action takes place heat is always produced by friction, and in all cases where heat is generated some of it will be lost by conduction, radiation and convection, tending to equalize the temperature of surrounding bodies. It is evident that heat so carried away is unavailable for further use, so

that in all manifestations of energy there is some lost or dissipated.

The more closely the investigation is followed in this direction, the more completely is the truth of this principle rendered manifest. Thus Soret (*Comptes Rendus*, xlv. 301) transmitted a continuous electric current through portions of conductors which, like Ampère's wires (fig. 245), are free to obey their mutual impulse of attraction and repulsion; and he found that if the moveable conductors were allowed to approach each other in accordance with the direction of the attraction, a diminution of the intensity of the current is observed during the occurrence of this motion,—a portion of the intensity of the current being expended in the production of motion. If, on the other hand, a compulsory movement in opposition to the attraction is effected, the intensity of the current is increased during the act of movement.

Again the same observer found, as might indeed have been anticipated from Faraday's magneto-electric researches (311), that if a battery in connexion with a helix be in conducting communication with a galvanometer, the current through the galvanometer is reduced during the introduction of a soft iron core into the axis of the helix; but it is increased at the moment of withdrawing the iron core. The introduction of a non-magnetic substance, such as a core of copper, produces no sensible effect.

We have already traced briefly the evolution of electricity from chemical action; and Faraday has further shown that the electricity developed by friction in the ordinary electrical machine produces either a corresponding amount of magnetic action on the needle of the galvanometer, or an equivalent amount of chemical decomposition in electrolytes through which it is transmitted (297); whilst in the fusion of metallic wires we have evidence of its heating power, and in the electric spark we see its agency in producing light.

The experiments of Faraday, followed by those of other philosophers, have proved that the motion of a magnet of a given strength, under certain conditions, produces, in a closed metallic conductor, a definite current of electricity, and through the electricity thus set in motion, light, heat, and chemical action may be developed, as is beautifully shown in the magneto-electric machine (315).

On the other hand, heat may be made to develope electricity; and the thermo-multiplier (317) of Nobili and Melloni shows that the current of electricity which is produced is exactly proportioned, *cæteris paribus*, to the amount of heat by which it is excited.

The ignition of solid matter shows that heat may elicit light under favourable circumstances. It further appears that heat may excite chemical action; and as it may also give rise to a current of electricity, through that current of electricity it may produce the development of magnetism.

Light may produce important chemical actions, but these actions have only in a few cases been reduced to a form in which they can develope electricity, magnetism, or heat. The quantitative valuation of light, and its relation with the other forces, still remains to be wrought out. Indeed, the subject appears to offer a field for research, difficult, because as yet scarcely trodden, though full of interest and promise.

The reader who desires to pursue the subject of the mutual relations of different kinds of energy, is referred to an interesting essay on the subject by Grove, entitled *On the Correlation of the Physical Forces*. For further information on the other subjects which have been treated of in this chapter, in addition to the papers already quoted, the student is referred to the important series of memoirs by Faraday, published in the *Philosophical Transactions*, which have also been reprinted in a separate form; or to the *Treatises* of Becquerel and De La Rive on *Electricity and Magnetism*, and to Tyndall's work on *Heat considered as a Mode of Motion*.

APPENDIX.

Densities corresponding to Degrees of Baumé's Hydrometer for Liquids heavier than Water (Poggiale).

Degrees.	Density.	Degrees.	Density.	Degrees.	Density.	Degrees.	Density.
0	1·000	20	1·161	40	1·383	60	1·711
1	1·007	21	1·171	41	1·397	61	1·732
2	1·014	22	1·180	42	1·410	62	1·753
3	1·022	23	1·190	43	1·424	63	1·774
4	1·029	24	1·199	44	1·438	64	1·796
5	1·036	25	1·210	45	1·453	65	1·819
6	1·044	26	1·221	46	1·468	66	1·846
7	1·052	27	1·231	47	1·483	67	1·872
8	1·060	28	1·242	48	1·498	68	1·897
9	1·067	29	1·253	49	1·514	69	1·921
10	1·075	30	1·264	50	1·530	70	1·946
11	1·083	31	1·275	51	1·546	71	1·974
12	1·091	32	1·286	52	1·563	72	2·000
13	1·100	33	1·297	53	1·580	73	2·031
14	1·108	34	1·309	54	1·597	74	2·059
15	1·116	35	1·320	55	1·615		
16	1·125	36	1·332	56	1·634		
17	1·134	37	1·345	57	1·652		
18	1·143	38	1·357	58	1·671		
19	1·152	39	1·370	59	1·691		

Densities on Baumé's Scale for Liquids lighter than Water (Francœur).

Degrees.	Density.	Degrees.	Density.	Degrees.	Density.	Degrees.	Density.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	0·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·749
21	0·930	34	0·859	47	0·798	60	0·745
22	0·924	35	0·854	48	0·794		

The degrees of Twaddell's hydrometer are readily converted into their corresponding specific gravities by multiplying them by 5, and adding 1000. The following is a short table of

Degrees on Twaddell's Hydrometer, and the corresponding Densities.

Degrees.	Density.	Degrees.	Density.	Degrees	Density.	Degrees	Density.
1	1·005	8	1·040	15	1·075	22	1·110
2	1·010	9	1·045	16	1·080	23	1·115
3	1·015	10	1·050	17	1·085	24	1·120
4	1·020	11	1·055	18	1·090	25	1·125
5	1·025	12	1·060	19	1·095	26	1·130
6	1·030	13	1·065	20	1·100	27	1·135
7	1·035	14	1·070	21	1·105	28	1·140

English Weights and Measures.—Avoirdupois.

	Grains.	Drachms.	Ounces.	lb.	Qrs.	Cwt.	Tons.
Grain . .	1						
Drachm .	27·34	1					
Ounce . .	437·5	16	1				
Pound . .	7000	256	16	1			
Quarter .	196000	7168	448	28	1		
Cwt. . .	784000	28672	1792	112	4	1	
Ton . .	15680000	573440	35840	2240	80	20	1

Troy Weight.

	Grains.	Dwts.	Ounces.	lb.
Grain	1			
Pennyweight . .	24	1		
Ounce	480	20	1	
Pound	5760	240	12	1

1 cubic inch of distilled water in air at 62° F. = 252·336 grains.
1 cubic inch of distilled water *in vacuo* at 62° F. = 252·645 grains.

		Cubic inches.
1 Gallon	=	277·276
1 Pint	=	34·659
1 Fluid ounce	=	1·7329
1 Litre	=	61·02705
1 Cubic centimetre	=	0·06102705

1 Cubic inch = 16·386176 cubic centimetres.

1·00000 parts of gas at 32° F., 29·922 Bar. (also at 32°), become at 60° F., Bar. 30 inches (also at 60°) = 1·057007 parts.

Comparison of French and English Weights.

		Grains.		Oz. Av.		lb. Av.
1 Milligramme	=	0·015432				
1 Centigramme	=	0·154323				
1 Decigramme	=	1·543234				
1 Gramme*	=	15·432348				
1 Kilogramme	=	15432·3488	=	35·2739	=	2·2046213

Comparison of French and English Measures of Length.

		English Inches.		Feet.		Yards.
1 Millimetre	=	0·03937079				
1 Centimetre	=	0·3937079				
1 Decimetre	=	3·937079				
1 Metre†	=	39·37079	=	3·2808992	=	1·0936331
1 Kilometre	=	39370·79	=	3280·8992	=	1093·6331

The length of the platinum metre is estimated at the temperature of 32° F., the English standard yard at 62° F.

1 English inch is equal to 25·39954 millimetres.

To Reduce Grammes to Grains.

Log. grammes + ·1884320 + 1 = log. grains.

To Reduce Cubic Centimetres to Cubic Inches.

Log. cubic centimetres + (·7855224 − 2) = log. cubic inches.

To Reduce Millimetres to Inches.

Log. millimetres + (·5951741 − 2) = log. inches.

To Convert Grains into Grammes.

Log. grains + (·8115680 − 2) = log. grammes.

To Convert Cubic Inches into Cubic Centimetres.

Log. cubic inches + ·2144776 + 1 = log. cubic centimetres.

To Convert Inches into Millimetres.

Log. inches + ·4048259 + 1 = log. millimetres.

* This determination of the gramme was made from the kilogramme des Archives by Professor W. H. Miller, in fixing the national standards (*Phil. Trans.* 1856, 893).

† The metre, at the time that its length was fixed by the French Government, was supposed to be a ten-millionth part of a quadrant of a meridian circle of the earth passing through Dunkirk and Barcelona. Subsequent more extended geodetic measurements have shown that it differs from this by about $\frac{1}{1000}$ of its length. The standard platinum metre of Borda at 0° C. is equal to $\frac{39{\cdot}37079}{36}$ of the English bronze standard yard at 62° F.

For Conversion of Metrical into English Measures.

A. Length.

Metrical to English.

1. Millimetres to Inches.	2. Metres to Feet.
1 = 0·03937079	1 = 3·2808992
2 = 0·07874158	2 = 6·5617984
3 = 0·11811237	3 = 9·8426976
4 = 0·15748316	4 = 13·1235968
5 = 0·19685395	5 = 16·4044960
6 = 0·23622474	6 = 19·6853952
7 = 0·27559553	7 = 22·9662944
8 = 0·31496632	8 = 26·2471936
9 = 0·35433711	9 = 29·5280928
$25^{mm.}4$ = rather more than 1 inch.	

English to Metrical.

3. Inches to Millimetres.	4. Feet to Metres.
1 = 25·39954	1 = 0·30479449
2 = 50·79908	2 = 0·60958898
3 = 76·19862	3 = 0·91438347
4 = 101·59816	4 = 1·21917796
5 = 126·99770	5 = 1·52397245
6 = 152·39724	6 = 1·82876694
7 = 177·79678	7 = 2·13356143
8 = 203·19632	8 = 2·43835592
9 = 228·59586	9 = 2·74315041
4 inches = rather more than $10^{cm.}$	

B. Capacity.

Metrical to English.

1. Cubic Centimetres to Cubic Inches.	2. Litres to Fluid Ounces.	3. Litres to Pints.	4. Litres to Gallons.
1 = 0·06102705	1 = 35·215468	1 = 1·7607734	1 = 0·22009668
2 = 0·12205410	2 = 70·430936	2 = 3·5215468	2 = 0·44019336
3 = 0·18308115	3 = 105·646404	3 = 5·2823202	3 = 0·66029004
4 = 0·24410820	4 = 140·861872	4 = 7·0430936	4 = 0·88038672
5 = 0·30513525	5 = 176·077340	5 = 8·8038670	5 = 1·10048340
6 = 0·36616230	6 = 211·292808	6 = 10·5646404	6 = 1·32058008
7 = 0·42718935	7 = 246·508276	7 = 12·3254138	7 = 1·54067676
8 = 0·48821640	8 = 281·723744	8 = 14·0861872	8 = 1·76077344
9 = 0·54924345	9 = 316·939212	9 = 15·8469606	9 = 1·98087012

The capacity of a litre is that of a cube each side of which is a decimetre.

English to Metrical.

1. Cubic Inches to Cubic Centimetres.	2. Fluid Ounces to Cubic Centimetres.	3. Pints to Litres.	4. Gallons to Litres.
1 = 16·386176	1 = 28·396612	1 = 0·567932	1 = 4·543458
2 = 32·772352	2 = 56·793224	2 = 1·135864	2 = 9·086916
3 = 49·158528	3 = 85·189836	3 = 1·703796	3 = 13·630374
4 = 65·544704	4 = 113·586448	4 = 2·271728	4 = 18·173832
5 = 81·930880	5 = 141·983060	5 = 2·839660	5 = 22·717290
6 = 98·317056	6 = 170·379672	6 = 3·407592	6 = 27·270748
7 = 114·703232	7 = 198·776284	7 = 3·975524	7 = 31·804206
8 = 131·089408	8 = 227·172896	8 = 4·543456	8 = 36·347664
9 = 147·475584	9 = 255·569508	9 = 5·111388	9 = 40·891122

C. Weight.

Metrical to English.

1. Grammes to Grains.	2. Kilogrammes to Ounces.	3. Kilogrammes to Pounds.
1 = 15·4323488	1 = 35·27394	1 = 2·20462
2 = 30·8646976	2 = 70·54788	2 = 4·40924
3 = 46·2970464	3 = 105·82182	3 = 6·61386
4 = 61·7293952	4 = 141·09576	4 = 8·81848
5 = 77·1617440	5 = 176·36970	5 = 11·02310
6 = 92·5940928	6 = 211·64364	6 = 13·22772
7 = 108·0264416	7 = 246·91758	7 = 15·43234
8 = 123·4587904	8 = 282·19152	8 = 17·63696
9 = 138·8911392	9 = 317·46546	9 = 19·84158

A milligramme is about $\frac{1}{65}$ grain.

The weight of a gramme is that of a cubic centimetre of distilled water at 4° C. (39°·2 F.)

English to Metrical.

1. Grains to Grammes.	2. Ounces to Grammes.	3. Pounds to Kilogrammes.	4. Hundred Weights to Kilogrammes.
1 = 0·0647989	1 = 28·34954	1 = 0·45359265	1 = 50·8023768
2 = 0·1295978	2 = 56·69908	2 = 0·90718530	2 = 101·6047536
3 = 0·1943967	3 = 85·04862	3 = 1·36077795	3 = 152·4071304
4 = 0·2591956	4 = 113·39816	4 = 1·81437060	4 = 203·2095072
5 = 0·3239945	5 = 141·74770	5 = 2·26796325	5 = 254·0118840
6 = 0·3887934	6 = 170·09724	6 = 2·72155590	6 = 304·8142608
7 = 0·4535923	7 = 198·44678	7 = 3·17514855	7 = 355·6166376
8 = 0·5183912	8 = 226·79632	8 = 3·62874120	8 = 406·4190144
9 = 0·5831901	9 = 255·14586	9 = 4·08233385	9 = 457·2213912

Value of Millimetres in English Inches.

Millimetres.	English inches.	Millimetres.	English inches.	Millimetres.	English inches.
1 . .	0·03937079	45 . . .	1·7716	125 . . .	4·921
2 . .	0·07874158	50 . . .	1·968	130 . . .	5·118
3 . .	0·11811237	55 . . .	2·165	135 . . .	5·315
4 . .	0·15748316	60 . . .	2·362	140 . . .	5·512
5 . .	0·19685395	65 . . .	2·559	145 . . .	5·709
6 . .	0·23622474	70 . . .	2·756	150 . . .	5·906
7 . .	0·27559553	75 . . .	2·953	155 . . .	6·103
8 . .	0·31496632	80 . . .	3·149	160 . . .	6·299
9 . .	0·35433711	85 . . .	3·346	165 . . .	6·496
10 . .	0·39370790	90 . . .	3·543	170 . . .	6·693
15 . .	0·5906	95 . . .	3·740	175 . . .	6·890
20 . .	0·7874	100 . . .	3·937	180 . . .	7·087
25 . .	0·9842	105 . . .	4·134	185 . . .	7·284
30 . .	1·1811	110 . . .	4·331	190 . . .	7·480
35 . .	1·3779	115 . . .	4·528	195 . . .	7·677
40 . .	1·5748	120 . . .	4·724	200 . . .	7·874

Table of the corresponding Heights of the Barometer in Millimetres and English Inches.

Millimetres.	English inches.	Millimetres.	English inches.	Millimetres.	English inches.
720 =	28·347	739 =	29·095	758 =	29·843
721 =	28·386	740 =	29·134	759 =	29·882
722 =	28·425	741 =	29·174	760 =	29·922
723 =	28·465	742 =	29·213	761 =	29·961
724 =	28·504	743 =	29·252	762 =	30·001
725 =	28·544	744 =	29·292	763 =	30·040
726 =	28·583	745 =	29·331	764 =	30·079
727 =	28·622	746 =	29·371	765 =	30·119
728 =	28·662	747 =	29·410	766 =	30·158
729 =	28·701	748 =	29·449	767 =	30·197
730 =	28·741	749 =	29·489	768 =	30·237
731 =	28·780	750 =	29·528	769 =	30·276
732 =	28·819	751 =	29·567	770 =	30·316
733 =	28·859	752 =	29·607	771 =	30·355
734 =	28·898	753 =	29·646	772 =	30·394
735 =	28·938	754 =	29·686	773 =	30·434
736 =	28·977	755 =	29·725	774 =	30·473
737 =	29·016	756 =	29·764	775 =	30·512
738 =	29·056	757 =	29·804		

Table for the Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
—100	— 148·0	— 49	— 56·2	2	35·6	53	127·4
— 99	— 146·2	— 48	— 54·4	3	37·4	54	129·2
— 98	— 144·4	— 47	— 52·6	4	39·2	55	131·0
— 97	— 142·6	— 46	— 50·8	5	41·0	56	132·8
— 96	— 140·8	— 45	— 49·0	6	42·8	57	134·6
— 95	— 139·0	— 44	— 47·2	7	44·6	58	136·4
— 94	— 137·2	— 43	— 45·4	8	46·4	59	138·2
— 93	— 135·4	— 42	— 43·6	9	48·2	60	140·0
— 92	— 133·6	— 41	— 41·8	10	50·0	61	141·8
— 91	— 131·8	— 40	— 40·0	11	51·8	62	143·6
— 90	— 130·0	— 39	— 38·2	12	53·6	63	145·4
— 89	— 128·2	— 38	— 36·4	13	55·4	64	147·2
— 88	— 126·4	— 37	— 34·6	14	57·2	65	149·0
— 87	— 124·6	— 36	— 32·8	15	59·0	66	150·8
— 86	— 122·8	— 35	— 31·0	16	60·8	67	152·6
— 85	— 121·0	— 34	— 29·2	17	62·6	68	154·4
— 84	— 119·2	— 33	— 27·4	18	64·4	69	156·2
— 83	— 117·4	— 32	— 25·6	19	66·2	70	158·0
— 82	— 115·6	— 31	— 23·8	20	68·0	71	159·8
— 81	— 113·8	— 30	— 22·0	21	69·8	72	161·6
— 80	— 112·0	— 29	— 20·2	22	71·6	73	163·4
— 79	— 110·2	— 28	— 18·4	23	73·4	74	165·2
— 78	— 108·4	— 27	— 16·6	24	75·2	75	167·0
— 77	— 106·6	— 26	— 14·8	25	77·0	76	168·8
— 76	— 104·8	— 25	— 13·0	26	78·8	77	170·6
— 75	— 103·0	— 24	— 11·2	27	80·6	78	172·4
— 74	— 101·2	— 23	— 9·4	28	82·4	79	174·2
— 73	— 99·4	— 22	— 7·6	29	84·2	80	176·0
— 72	— 97·6	— 21	— 5·8	30	86·0	81	177·8
— 71	— 95·8	— 20	— 4·0	31	87·8	82	179·6
— 70	— 94·0	— 19	— 2·2	32	89·6	83	181·4
— 69	— 92·2	— 18	— 0·4	33	91·4	84	183·2
— 68	— 90·4	— 17	+ 1·4	34	93·2	85	185·0
— 67	— 88·6	— 16	3·2	35	95·0	86	186·8
— 66	— 86·8	— 15	5·0	36	96·8	87	188·6
— 65	— 85·0	— 14	6·8	37	98·6	88	190·4
— 64	— 83·2	— 13	8·6	38	100·4	89	192·2
— 63	— 81·4	— 12	10·4	39	102·2	90	194·0
— 62	— 79·6	— 11	12·2	40	104·0	91	195·8
— 61	— 77·8	— 10	14·0	41	105·8	92	197·6
— 60	— 76·0	— 9	15·8	42	107·6	93	199·4
— 59	— 74·2	— 8	17·6	43	109·4	94	201·2
— 58	— 72·4	— 7	19·4	44	111·2	95	203·0
— 57	— 70·6	— 6	21·2	45	113·0	96	204·8
— 56	— 68·8	— 5	23·0	46	114·8	97	206·6
— 55	— 67·0	— 4	24·8	47	116·6	98	208·4
— 54	— 65·2	— 3	26·6	48	118·4	99	210·2
— 53	— 63·4	— 2	28·4	49	120·2	100	212·0
— 52	— 61·6	— 1	30·2	50	122·0	101	213·8
— 51	— 59·8	0	32·0	51	123·8	102	215·6
— 50	— 58·0	+ 1	33·8	52	125·6	103	217·4

Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

[*Continued.*]

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
104	219·2	155	311·0	206	402·8	257	494·6
105	221·0	156	312·8	207	404·6	258	496·4
106	222·8	157	314·6	208	406·4	259	498·2
107	224·6	158	316·4	209	408·2	260	500·0
108	226·4	159	318·2	210	410·0	261	501·8
109	228·2	160	320·0	211	411·8	262	503·6
110	230·0	161	321·8	212	413·6	263	505·4
111	231·8	162	323·6	213	415·4	264	507·2
112	233·6	163	325·4	214	417·2	265	509·0
113	235·4	164	327·2	215	419·0	266	510 8
114	237·2	165	329·0	216	420·8	267	512·6
115	239·0	166	330·8	217	422·6	268	514·4
116	240·8	167	332·6	218	424·4	269	516·2
117	242·6	168	334·4	219	426·2	270	518·0
118	244·4	169	336·2	220	428·0	271	519·8
119	246·2	170	338·0	221	429·8	272	521·6
120	248·0	171	339·8	222	431·6	273	523·4
121	249·8	172	341·6	223	433·4	274	525·2
122	251·6	173	343·4	224	435·2	275	527·0
123	253·4	174	345·2	225	437·0	276	528·8
124	255·2	175	347·0	226	438·8	277	530·6
125	257·0	176	348·8	227	440·6	278	532·4
126	258·8	177	350·6	228	442·4	279	534·2
127	260 6	178	352·4	229	444·2	280	536·0
128	262·4	179	354·2	230	446·0	281	537·8
129	264·2	180	356·0	231	447·8	282	539·6
130	266·0	181	357·8	232	449·6	283	541·4
131	267·8	182	359·6	233	451·4	284	543·2
132	269 6	183	361·4	234	453·2	285	545·0
133	271·4	184	363·2	235	455·0	286	546·8
134	273·2	185	365 0	236	456·8	287	548·6
135	275·0	186	366·8	237	458·6	288	550·4
136	276·8	187	368·6	238	460·4	289	552·2
137	278·6	188	370·4	239	462·2	290	554·0
138	280·4	189	372·2	240	464 0	291	555·8
139	282·2	190	374 0	241	465·8	292	557·6
140	284·0	191	375·8	242	467·6	293	559·4
141	285·8	192	377·6	243	469·4	294	561·2
142	287·6	193	379·4	244	471·2	295	563·0
143	289·4	194	381·2	245	473·0	296	564·8
144	291·2	195	383·0	246	474·8	297	566·6
145	293·0	196	384·8	247	476·6	298	568·4
146	294·8	197	386·6	248	478·4	299	570·2
147	296·6	198	388·4	249	480·2	300	572·0
148	298·4	199	390·2	250	482·0	301	573 8
149	300·2	200	392·0	251	483·8	302	575·6
150	302·0	201	393·8	252	485·6	303	577·4
151	303·8	202	395·6	253	487·4	304	579·2
152	305·6	203	397·4	254	489·2	305	581·0
153	307·4	204	399·2	255	491·0	306	582·8
154	309·2	205	401·0	256	492·8	307	584·6

Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

[*Continued.*]

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
308	586·4	333	631·4	358	676·4	704·4	1300
309	588·2	334	633·2	359	678·2	760	1400
310	590·0	335	635·0	360	680·0	800	1472
311	591·8	336	636·8	370	698	815·6	1500
312	593·6	337	638·6	371·1	700	871·1	1600
313	595·4	338	640·4	380	716	900	1652
314	597·2	339	642·2	390	734	926·7	1700
315	599·0	340	644·0	400	752	982·2	1800
316	600·8	341	645·8	410	770	1000	1832
317	602·6	342	647·6	420	788	1037·8	1900
318	604·4	343	649·4	426·7	800	1093·3	2000
319	606·2	344	651·2	430	806	1100	2012
320	608·0	345	653·0	440	824	1148·8	2100
321	609·8	346	654·8	450	842	1200	2192
322	611·6	347	656·6	460	860	1300	2372
323	613·4	348	658·4	470	878	1400	2552
324	615·2	349	660·2	480	896	1500	2732
325	617·0	350	662·0	482·2	900	1600	2912
326	618·8	351	663·8	490	914	1700	3092
327	620·6	352	665·6	500	932	1800	3272
328	622·4	353	667·4	537·8	1000	1900	3452
329	624·2	354	669·2	593·3	1100	2000	3632
330	626·0	355	671·0	600	1112	2100	3812
331	627·8	356	672·8	648·9	1200	2200	3992
332	629·6	357	674·6	700	1292	2300	4172

Without Correction for 0°.

° C. Contain ° F.	° F. Contain ° C.
1 = 1·8	1 = 0·55
2 = 3·6	2 = 1·11
3 = 5·4	3 = 1·66
4 = 7·2	4 = 2·22
5 = 9·0	5 = 2·77
6 = 10·8	6 = 3·33
7 = 12·6	7 = 3·88
8 = 14·4	8 = 4·44
9 = 16·2	9 = 5·00

Table of the Pressure of Aqueous Vapour expressed in Inches of Mercury, at 32° F., *for each degree* F. *between* 0° *and* 100°. *From Dixon's 'Treatise on Heat'* (p. 257). *Regnault.*

Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.
0	0·0439	26	0·1395	51	0·3742	76	0·8964
1	0·0459	27	0·1457	52	0·3882	77	0·9266
2	0·0481	28	0·1522	53	0·4026	78	0·9577
3	0·0503	29	0·1589	54	0·4175	79	0·9898
4	0·0526	30	0·1660	55	0·4329	80	1·0227
5	0·0551	31	0·1733	56	0·4488	81	1·0566
6	0·0576	32	0·1810	57	0·4653	82	1·0915
7	0·0603	33	0 1883	58	0·4822	83	1·1274
8	0·0630	34	0·1959	59	0·4997	84	1·1643
9	0·0659	35	0·2038	60	0·5178	85	1·2023
10	0·0689	36	0·2119	61	0·5364	86	1·2413
11	0·0721	37	0 2204	62	0·5556	87	1·2815
12	0·0753	38	0·2291	63	0·5755	88	1·3228
13	0·0788	39	0 2381	64	0·5959	89	1·3652
14	0 0823	40	0·2475	65	0·6170	90	1·4088
15	0·0861	41	0·2571	66	0·6388	91	1·4537
16	0·0899	42	0·2672	67	0·6612	92	1·4998
17	0·0940	43	0·2775	68	0·6843	93	1·5471
18	0·0982	44	0·2882	69	0·7081	94	1·5958
19	0·1027	45	0·2993	70	0·7327	95	1·6457
20	0·1073	46	0·3108	71	0·7580	96	1·6971
21	0·1121	47	0·3226	72	0·7841	97	1·7498
22	0·1171	48	0·3349	73	0·8109	98	1·8039
23	0·1223	49	0·3476	74	0·8386	99	1·8595
24	0·1278	50	0·3607	75	0·8671	100	1·9170
25	0·1335						

Pressure of Aqueous Vapour in Millimetres of Mercury for each degree C. *between* 0° *and* 35° (*Regnault*).

°	Mm.	°	Mm.	°	Mm.
0	4·600	12	10·457	24	22·184
1	4·940	13	11·162	25	23·550
2	5·302	14	11·908	26	24·988
3	5·687	15	12·699	27	26·505
4	6·097	16	13·536	28	28·101
5	6·534	17	14 421	29	29·782
6	6·998	18	15·357	30	31·548
7	7·492	19	16·346	31	33 406
8	8·017	20	17·391	32	35·359
9	8·574	21	18·495	33	37·411
10	9·165	22	19·659	34	39·565
11	9·792	23	20·888	35	41·827

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